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CONTENTS

SOIL–PLANT-DISEASE RELATIONSHIPS

The papers contained in this issue of SOIL SCIENCE were prepared by invitation of the editors for the purpose of presenting an over-all picture of the problems involved in the control of plant disease organisms that harbor in the soil and the means employed by plant pathologists to control them.

The authors of these papers were chosen, with the help of their colleagues, because of their special researches in those portions of this field of endeavor with which their papers are primarily concerned. They are in position, therefore, to speak with authority on the subjects assigned to them. Each author was asked to present a general review of the literature of his subject and to add such additional data as might have been obtained under his direction since his next previous paper was published.

The fact that this issue of SOIL SCIENCE was to be devoted to soil–plant-disease relationships was brought to the attention of all plant pathologists with the cordial cooperation of the editors of *Phytopathology* by the publication of an announcement in their Journal. It is hoped and believed that many soil scientists as well will find material of considerable value in these papers, not the least of which are the excellent bibliographies that are appended.

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SOIL AS A MEDIUM FOR TRANSFER AND MULTIPLICATION OF DISEASE ORGANISMS

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Any soil-borne plant parasite is involved in two principal biological relationships—that with its host plant, and that with the other members of the soil population. The evolution of the parasitic habit in root-infecting fungi, with which group of organisms this article is chiefly concerned, has been affected no less by the second than by the first of these relationships. In the early days of plant pathology, however, investigators were preoccupied with the host–parasite relationship to the exclusion of most other considerations. Just as ontogeny is said to repeat phyllogeny, so the course of investigation of a new root disease reflects the developmental phases in the history of root disease investigation in general. Determination of the primary parasite is the first essential step toward elucidating the epidemiology of any soil-borne disease. The parasites responsible for most of the principal root diseases of crop plants were determined in the second half of the nineteenth century, though some few were not correctly named until the first and second decades of the twentieth century. Shortly before the beginning of the third decade, plant pathologists turned from their intensive studies of the host–parasite relationship to consider the influence of the environment upon disease development. This new trend in investigation must be credited chiefly to L. R. Jones and the Wisconsin school of plant pathology. The invention of the famous Wisconsin soil temperature tanks made possible the accurate measurement of the effect of soil temperature and moisture content upon development of disease; the experimental results thus obtained proved to be invaluable for the interpretation of field records on the seasonal occurrence and geographical distribution of soil-borne diseases in the United States (6).

Last but not least of the soil factors to receive adequate recognition of its influence upon the root-infecting fungi was the microbiological factor. Interest in microbiological antagonism as a potential force for the control of soil-borne diseases grew apace after the dramatic demonstration by Millard and Taylor (9) in 1927 that development of scab on potatoes grown in sterilized soil inoculated with *Actinomyces scabies* could be reduced by simultaneous inoculation of the soil with *A. praecox*, an obligate saprophyte of a more vigorous habit of growth. Millard and Taylor were not the first to suggest that the control of potato scab by green manuring was due to the antagonism toward *A. scabies* of organisms multiplying on the green manure, for such a suggestion had been put forward by Sanford (15) in the previous year. Indeed, the recognition of microbiological antagonism as an important factor in the soil environment of plant parasites was due largely to the work of Sanford (16), and to that of another Canadian investigator, A. W. Henry. By his masterly experimental analysis of the interrelation between soil temperature and microbiological antagonism

toward *Ophiobolus graminis*, Henry (5) in 1932 was able to explain the anomalous effect of low soil temperature in encouraging development of the take-all disease in wheat seedlings, previously reported by McKinney and Davis (8). In the same year, Weindling (21) published the first of a series of papers in which he demonstrated the parasitism of a common soil fungus, *Trichoderma lignorum*, upon the plant pathogen *Rhizoctonia solani*. His investigation of the mechanism of this parasitism, and of the toxin or "lethal principle" excreted by *T. lignorum*, probably served, more than any other, to demonstrate the potentialities of antibiosis for control of soil-borne plant diseases. More than a promise, however, was held out by King *et al.* (7), who in 1934 reported successful control of *Phymatotrichum omnivorum* root-rot in continuous cotton by heavy annual applications of organic manures; their experiments were carried out in the field, and there was thus no doubt concerning the relation to actual practice. The mechanism of this control, which King *et al.* attributed to the microbiological antagonism toward *P. omnivorum* of the organisms multiplying on the organic manures, has been further analyzed by Mitchell *et al.* (10) and by Clark (2). The mechanisms of such microbiological antagonism are likely to be both diverse and complex, and much more experimental analysis is required before methods of so-called "biological control" can be worked out to the best advantage for individual soil-borne diseases.

A more fundamental estimate of the relationship between the root-infecting fungi and other members of the soil microflora was reached in another way, through ecological studies of the fungus flora of the soil. In this sphere of soil microbiology, as in others, we are indebted to S. A. Waksman for a fundamental conception which has much influenced subsequent work. As a result of a survey of fungi in soils taken from different parts of the North American continent, and from the results of European investigators, Waksman (18) in 1917 concluded that there is a cosmopolitan fungus flora of regular *soil inhabitants*. Among this flora of soil inhabitants, however, Waksman found casual or exotic fungi, which he termed *soil invaders*. Some fifteen years after the publication of Waksman's paper, work on the Panama disease of bananas in Central America led Reinking and Manns (11, 12, 13) to conclusions of far-reaching importance concerning the ecology of the root-infecting fungi. After an extensive search for species of *Fusarium* in the soils of Central America, Reinking and Manns found that some *Fusarium* species were present in all, or nearly all, the soils examined. These they called, following Waksman, *soil inhabitants*. Other species, however, had only a local distribution, which apparently coincided with the distribution of host plants. With the death of its host plant, the local population of such a plant parasitic *Fusarium* gradually dwindled, until it eventually disappeared from the soil. Such locally distributed species of *Fusarium* were named, again following Waksman, *soil invaders*.

Garrett (3) deemed Reinking and Manns' conception of such importance that he further developed it to distinguish between two contrasting types of behavior in the whole group of root-infecting fungi, insofar as the ecology of

these organisms was then known. Garrett epitomized the behavior of these two contrasting groups as follows:

The soil inhabitants are considered to be primitive or unspecialised parasites with a wide host range; these fungi are distributed throughout the soil, and their parasitism appears to be incidental to their saprophytic existence as members of the general soil microflora. The *soil invaders*, to which class the majority of the root-infecting fungi seem to belong, are more highly specialized parasites; the presence of such fungi in the soil is generally closely associated with that of their host plants. In the continued absence of a host plant, such fungi die out in the soil, owing to their inability to compete with the soil saprophytes for an existence on non-living organic matter. This close association between the *soil invaders* and their host plants thus seems to be enforced by the competition of the general soil microflora.

If competition is the factor governing evolution of the root-infecting fungi, as it is believed to be in other groups of organisms, then evolution of the root-infecting habit may be regarded as an *escape* from the intense struggle for saprophytic existence in the soil (4). The root-infecting fungi, as a group, may thus be deemed analogous to those groups of specialized higher plants that have *escaped* from the intense competition characteristic of favorable habitats by virtue of their ability to colonize such poor habitats as sand dunes, shingle banks, and bare rock faces.

Enough has been said to indicate that mere ability of any particular root-infecting fungus to grow as a saprophyte in pure culture is no criterion whatsoever of its ability to live as a saprophyte in the soil. As Waksman (19) has pointed out in many contexts, the dominant microorganisms decomposing any substrate under any particular set of environmental conditions are the organisms best fitted to decompose that particular substrate under those particular environmental conditions. For each microorganism, therefore, there must be an optimum habitat, be it wide or narrow in extent, and to this habitat the organism is more or less restricted by pressure of competition. The organic material on which fungi and all other heterotrophic soil microorganisms must exist is provided by the bodies of plants and animals. As such substrates progressively change with the course of decomposition, so the decomposing microflora must change also. The *succession* of microorganisms developing on such an organic substrate is thus analogous to the succession of organisms developing on a newly exposed habitat aboveground. The validity of this analogy is not affected by the obvious differences between the two types of succession. Competition among surface vegetation aboveground is for space and light, belowground for root hold and root space, and the end point of the succession is the climax association, or most highly developed plant community that the habitat can support. Competition among soil microorganisms, on the other hand, is for organic substrates, which are finite and therefore exhaustible; the end point of the succession on individual substrates is thus zero.

It follows, therefore, that both a *spatial* and a *temporal distribution* of any particular soil microorganism on organic substrates can be envisaged (4). The spatial distribution is determined by the kinds of habitats that the micro-

organism can colonize under competition, *habitat* being defined as the sum total of the environmental factors, including the organic substrate. By temporal distribution is implied the period or periods of time for which the microorganism can exist upon the substrate during its decline from living plant or animal tissue to zero. This distinction is illustrated by the behavior of various species of root-infecting fungi. The fungus *Ophiobolus graminis*, causing the take-all disease of cereals, is a typical highly specialized parasite of the soil-invader type. It spreads and multiplies in the soil only on the roots of living graminaceous host plants. Its saprophytic life is limited to a somewhat precarious tenancy of the plant tissues that it has invaded as a parasite; it is unable to colonize fresh dead plant tissues in the soil in competition with more vigorous saprophytes (which also tend to suppress its development on plates of nutrient agar when surface-sterilized pieces of infected plant tissue are plated out). In contrast, the fungus *Fusarium culmorum* appears to be a primitive parasite of the soil-inhabitant type. Thus Sadasivan (14) and Walker (20) have shown that this fungus, though of minor importance as a primary parasite of wheat in Great Britain, frequently follows *Ophiobolus graminis* as a secondary parasite, and that it is also one of the primary fungal colonizers of healthy wheat roots and straw left in the soil after harvest. Prominent among other primary colonizers of healthy wheat straw were found species of *Penicillium;* unlike *F. culmorum*, these seemed to be wholly saprophytes, and were unable to parasitize cereal plants even in the seedling stage.

The tropical species of *Rosellinia* have been cited (4) as the best example of the primitive parasites which are classed as soil inhabitants. These fungi are typically saprophytes living in the surface humus layer of rain forest floors, where surface litter accumulates under conditions of high rainfall and dense shade. These species of *Rosellinia* can be considered as primitive parasites insofar as they quickly kill the woody host plants that they chance to encounter. More highly specialized parasites are characterized by a more delicately adjusted relationship with their host, which tends in the direction of symbiosis, as exemplified by the mycorrhizal fungi. Another example, more familiar to observers in temperate countries, of a primitive parasite of soil-inhabitant status, is afforded by the common *Pythium deBaryanum*, causing damping-off of seedlings. Some mycologists might, however, deny that this fungus is a parasite at all, as it kills the seedling tissues in advance of penetration, and is thus living as a saprophyte in already killed cells.

Some interesting questions concerning the saprophytic activity of a root-infecting fungus are posed by the recent work of Blair (1) on *Rhizoctonia solani*. This fungus is a well-known root and stem parasite, albeit of a relatively primitive type, of many plants. Blair demonstrated that *R. solani* was capable of making a free and independent saprophytic growth through untreated field soil. Such soil must have contained sufficient residual organic matter in the form of "humus" to support growth of the fungus. Nevertheless, the growth of *R. solani* was actually suppressed by addition to the soil of fresh organic material, such as 1 per cent of ground dried grass. Blair showed that this suppression was

due to the development upon the organic material of other soil microorganisms; he further demonstrated that *R. solani* possessed only a low capacity for cellulose decomposition in comparison with that of some other saprophytic soil fungi. In *R. solani*, therefore, we have a fungus which may have two periods of activity during the course of disintegration of plant tissue: first, as a parasite in the first stage; and second, as a saprophyte on residual humus in the penultimate stage of decomposition.

The possibility of such differences in saprophytic behavior among the soil fungi was perceived by Thom and Morrow (17) when they wrote in 1937: "Soil fungi may possibly be divided into two sections: first, those capable of living normally in relation to soil organic matter in the chemical sense, *i.e.*, to residual products of decomposition; and second, those concerned in primary decomposition, *i.e.* the breakdown of plant and animal remains towards those residual products." The field of research thus discerned by Thom and Morrow offers a prospect full of interest for further exploration.

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SOIL-BORNE DISEASES IN RELATION TO THE MICROFLORA ASSOCIATED WITH VARIOUS CROPS AND SOIL AMENDMENTS[1]

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During recent years the plant pathologists' viewpoint regarding the development of soil-borne diseases of crop plants has changed considerably. There has been a greater tendency to appreciate the various influences exerted by the associated microflora on the growth and persistence of the pathogen, correspondingly less weight being placed on such factors as soil temperature, moisture content, aeration, and reaction.

The chief cause of the change in viewpoint was the experimental demonstration (11, 21, 25) that a relatively large number of cultures of common soil-inhabiting bacteria and fungi, or their filtrates, when added to a soil containing the pathogen, reduced or suppressed the development of disease. Naturally this discovery at once suggested the possibility of practical biological control of disease, as well as the need for a more complete picture of the effects on the associated soil microflora of different crops, cultural practices, and soil amendments. A soil microbiological approach to the problem thus became necessary (26).

The generally beneficial effect of crop sequence and summer fallow in reducing soil-borne diseases is well recognized, but the "mechanism" involved is a mystery. For instance, it is not known whether the normal growth of the pathogen suffers because essential growth substances are not elaborated by the living nonhost plant or its characteristic rhizosphere microflora, or whether certain members of the latter are strongly antibiotic or even parasitic to the pathogen. In the case of summer fallow or in the addition of organic matter and other soil amendments to an infested soil, is the mechanism of control essentially the same as that for a nonhost crop, or, is it different? Whatever the general "mechanism" is, it seems probable that the reaction of the various pathogens, or their strains, might be different—a reason for studying critically the response of each pathogen.

This paper reviews briefly certain data on relevant aspects of five typical soil-borne diseases and discusses briefly the possible relation of the rhizosphere to disease incidence. These diseases are common scab [*Actinomyces scabies* (Thaxter) Güssow] and stem canker (*Rhizoctonia solani* Kühn) of the potato; take-all (*Ophiobolus graminis* Sacc.) and common root rot [*Helminthosporium sativum* P. K., & B., and *Fusarium culmorum* (W. G. Sm.) Sacc.] of wheat. The two potato pathogens do not attack the roots in natural soil and are not directly dependent on the roots for survival, whereas the wheat pathogens attack both roots and the underground part of the stem. With the exception

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of *O. graminis*, all are vigorous soil saprophytes capable of persisting without the host.

COMMON SCAB OF POTATO (*A. scabies*)

In an attempt to discover the reason for the observed erratic incidence of potato scab under field conditions, the writer found that the severity of the disease could be reduced by raising the water content of the soil. But a study (24) of the relative importance of the moisture content of the soil, temperature, aeration, substrate reaction, and effect of green rye, as well as various bacterial associates on the pathogen, led to the conclusion that, under field conditions, the severity of the disease might often be modified by the antagonistic effects of associated soil microorganisms. This general conclusion was subsequently confirmed by the work of Millard and Taylor (19), Dippenaar (5), Goss (9), and others. It is well known that common scab is seldom troublesome in soils below pH 5. Between pH 5 and pH 8, however, it may be either extremely severe or of little importance, despite favorable temperature, soil reaction, and other conditions, or, in some instances, it may respond to certain crop rotations (8) or soil amendments.

Instances have been reported of control of common scab (9) and other diseases by the use of organic manure. For example, King *et al.* (14) found that the cotton root-rot fungus, *Phymatotrichum omnivorum*, was less abundant in manured than in unmanured soils, whereas the opposite was true of saprophytic microorganisms. These workers concluded that the manure favored the development of an antagonistic microflora and recommended the continuous application of manures as a practical control measure.

Experimental data (table 1) obtained during 1932 and 1933, but hitherto unpublished, suggest some aspects of microbiological antagonism, as well as the possible value of adding plant material to soil to reduce common scab. The tests were made in very heavily infested steam-sterilized and natural black loam soil, mixed with finely chopped green rye or clover at the rate of 30 tons per acre. This inoculated soil-plant compost was placed in the field in round holes, 15 inches in diameter and 6 inches deep. A disinfected potato set of the Cobbler variety was planted in each hole. Throughout the season the soil reaction did not vary significantly from its initial value of pH 6.2. The data in the first test show that the disease in the natural soil series was more than twice as severe as it was in the sterilized soil, and in the second test five times as severe. The addition of either rye or clover to the natural soil depressed the virulence of the pathogen by 17 per cent and 8 per cent for the rye and clover, respectively, in the first test, and by 30 per cent and 49 per cent in the second. Since the temperature, water content, aeration, and reaction of the soil were favorable for disease incidence, it was assumed that the differences noted in the various treatments were expressions of antibiotic activity of the associated soil microflora.

Typical data from an unfinished study begun in 1935 (table 2) show how markedly antibiotic certain soil-inhabiting bacteria can be to *A. scabies* in a

soil substrate. Briefly, the procedure was to mix spores of *A. scabies* in the steam-sterilized soil (pH 6.2) of optimum water content and, with the aid of a specially designed metal scoop, to place this inoculated soil inside deep Petri plates, each containing a thin layer of potato dextrose agar. The surface of

TABLE 1

Common scab of potato on tubers grown in natural and sterilized soil artificially infested with A. scabies and mixed with green rye or clover plants at the rate of 30 tons per acre

TREATMENT* OF SOIL	AVERAGE YIELD PER HILL	DISEASE RATING PER HILL†								
		1	2	3	4	5	6	7	8	Av.
	lbs.	%	%	%	%	%	%	%	%	%
Experiment I, 1932										
NIR	3.5	20	0	50	30	50	30	40	50	34
SIR	4.3	..	30	20	20	30	20	20	30	24
NI	4.2	20	70	50	50	60	50	60	50	51
SI	4.9	20	10	20	20	30	20	40	20	23
NIC	3.2	30	..	50	30	60	30	..	60	43
SIC	3.8	20	30	50	30	..	50	20	20	31
S	4.5	0	0	0	0	0	0	0	0	0
Experiment II, 1933										
NIR	2.6	40	..	70	80	40	40	10	10	41
SIR	3.3	30	35	20	0	20	0	..	30	19
NI	3.5	80	15	90	50	90	90	70	80	71
SI	3.9	15	10	10	5	40	5	10	10	13
NIC	2.1	40	..	..	35	30	..	5	0	22
SIC	3.0	..	..	30	0	..	15	20	5	14
S	3.7	0	0	0	0	0	0	0	0	0

* N, I, S, R, C = Natural; Infested; Sterilized; Rye and Clover, finely chopped green material mixed with the soil at the rate of 30 tons per acre, respectively.
† Leaders indicate rotted sets.

the soil was then lightly touched in several places with the loop of an inoculating needle containing a bacterial or fungal culture. These uncontaminated plates were incubated at room temperature.

The data in table 2 and figure 1 show that the growth of *A. scabies* in a soil medium may be greatly suppressed, and in some instances killed, by certain associated common soil-inhabiting bacteria, and that little or no ill effect may be exerted by others. The cultures of fungi were representative of genera known to be most prevalent in normal soils and particularly abundant in the presence of decaying plant material and stable manure and also in recolonizing steam-

sterilized soil. Apparently none of them was markedly antibiotic to *A. scabies*, although it is possible that other strains might have been.

TABLE 2

Growth* of A. scabies, R. solani, and H. sativum as affected by different soil-inhabiting bacteria and fungi in a sterilized soil medium

TIME	TEST	BACTERIAL CULTURES						FUNGI†				CONTROL
		B2	B10	B12	B16	B17	B19	F50	F52	F53	F62	
days		%	%	%	%	%	%	%	%	%	%	%
		A. scabies										
6		80	60	60	0	0‡	0‡	80	55	60	80	100
12		90	70	60	5	0‡	0‡	85	65	75	85	100
20		95	85	65	20	0‡	0‡	90	70	85	90	100
		R. solani§										
9		*100*	*100*	*100*	*40*	*40*	*0*					*100*
	1st	100	100	100	40	40	40					100
	2nd	100	100	100	60	60	60					100
		H. sativum§										
9		*90*	*90*	*90*	*40*	*40*	*20*					*100*
	1st	100	100	100	80	80	80					100
	2nd	100	100	100	90	90	90					100

* Average of 5 plates.

† F50, *Mucor* sp.; F52, *Trichoderma lignorum;* F53, *Penicillium* sp.; F62, *Aspergillus niger.* (Different methods used for testing these and other fungi.)

‡ Recovery of *A. scabies* impossible.

§ Italic figures indicate growth on potato dextrose agar.
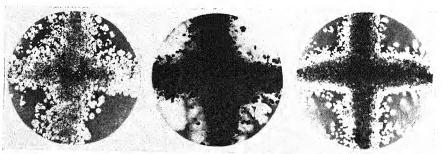
FIG. 1. EFFECT OF TWO DIFFERENT BACTERIAL CULTURES ON GROWTH OF *Actinomyces scabies* IN SOIL

Left, control; center, *A. scabies* and B19; right, *A. scabies* and B10. Photographed after 12 days.

Let us now attempt to explain the results listed in table 1. On the whole, the data strongly indicate that the depression of virulence in the treated natural soil and in the sterilized soil minus plant material was due more to the qualitative

growth of the microflora as favored by the particular treatment than by the mere quantitative growth of fungi and bacteria. If this were not so, least virulence would be expected in the sterilized soil containing the green manure. In this soil, however, virulence was not significantly different from that in the untreated sterilized soil, which suggests that conditions in the latter soil were most favorable for the development of one or more kinds of bacteria, or possibly fungi, antibiotic to A. scabies. At any rate, there is no evidence that the growth of the microflora, as induced by the plant-soil mixture, was significantly more antibiotic. Possibly the plant material favored the development of a microflora similar to that of the sterilized soil, in which case the total effect would not necessarily be different. This assumption might also explain the marked fluctuations in disease severity which developed in some of the replicates of the various treatments.

Likewise, it is assumed that the stabilized microflora of the natural soil was fairly compatible to the growth and persistence of the inoculum, but with the addition of the rye and clover plant material some kinds of bacteria, and possibly certain fungi, in the rapidly increasing microflora were, in varying degrees, antibiotic to the pathogen. For the best development of the potato scab disease, the stability of the added inoculum over a period would seem to be of greater importance than mere amount of inoculum added at the beginning of a test. But the data do not indicate whether the major antibiotic effect developed at the beginning of the test and then declined gradually as the microflora became more stabilized, or whether bacteria or fungi were more important in the antibiosis produced. Light on the latter possibility might be highly significant in view of the evidence in table 2 and in figure 1.

In a similar experiment at the University Farm, Minnesota (24), during 1925, uniformly severe scab developed when chopped green rye, at the heavy rate of 50 tons per acre, was mixed with a naturally infested field soil of pH 5.2. The following comment was made, "If control can be obtained by its use in some soils it may be that certain microorganisms of the greatly increased soil microflora are antibiotic to A. scabies." Goss (9), in 1937, applied stable manure in a sterilized soil compost to a natural field soil, both heavily reinfested with inoculum of A. scabies, and obtained results comparable to those listed in table 1 for rye and clover manure. It should be emphasized, however, that he reported the greatest amount of potato scab in the untreated, sterilized soil, where the writer found the least disease (table 1). These, and other dissimilarities which may be expected in experiments of this kind, stress the danger as well as the difficulty of attempting to interpret or even compare results without all the facts.

POTATO STEM CANKER (R. solani)

Heald (10) has reviewed rather fully the literature dealing with the host range, life history, and pathogenic capabilities of R. solani as affected by soil temperature, moisture, reaction, and certain crop sanitation measures recommended to reduce the disease. Rhizoctonia solani has a very wide host range and unusual capacity to persist successfully within a relatively wide range of soil moisture or

cropping practice.   It is generally assumed that successive crops of given host plants tend to favor the increase of those races which parasitize the plants, and that when the host is absent the fungus tends to disappear.   This explanation does not seem wholly adequate, in view of the known saprophytic capabilities of *R. solani*, on the one hand, and the experimental evidence (table 2) of the possible role of antibiosis and related phenomena, on the other.

Weindling (36) showed that a diffusible toxic substance from *T. lignorum* was destructive to the mycelial cells of *R. solani*, when both were associated in artificial media.   Allen and Haenseler (1) found that the effective principle was not equally toxic on artificial media to all soil fungi.   Daines (4) found that the toxic principle elaborated by *T. lignorum* is rapidly destroyed in potato soils of pH 5.6 and is, therefore, ineffective in controlling the disease caused by *R. solani* or the potato scab fungus.   He suggested that antagonistic relationships apparent on artificial media might be modified or entirely lost in a soil medium. Cordon and Haenseler (3) showed that a diffusible, heat-stable substance produced on artificial media by *Bacillus simplex* completely suppressed the growth of *R. solani* in nutrient media at dilutions of 5 per cent of original strength, and reported "appreciable" control of damping-off of cucumbers and peas by treating the soil with the washed bacterial cells without the nutrient, and "some" control by applying the nutrient medium alone.   The data in table 2, obtained in a soil medium, show that different cultures of bacteria which almost or completely suppressed the growth of *A. scabies* also partly suppressed the growth of *R. solani*, whereas others having only an intermediate effect on *A. scabies* showed no detrimental effect on *R. solani*.   The writer is not aware of other confirmatory evidence of this kind as applied to *R. solani* in a soil medium, but it seems very probable that further study along this line would produce significantly positive results.   The point to keep in mind here is that under aseptic conditions there are soil-inhabiting bacteria which suppress the growth of *R. solani* to varying degrees in a steam-sterilized black loam soil, where growing roots or the dead remains of the host are absent.   It has not been shown whether the same or other antagonistic bacteria or fungi would be effective on the growth of *R. solani* in a natural soil.

The representative data in table 3, taken from an unpublished study of the effect in natural soil of various soil amendments on the virulence and persistence of *R. solani*, strongly suggest, however, that even here antibiosis may be very effective.   The experiment was performed in a cool (16°–17°C.), humid, temperature-controlled chamber, where it was necessary to add only a very slight amount of water to the soil at the end of the third and sixth plantings.   The initial inoculum was uniform in all replicates throughout.   Consequently, it is assumed that the striking variability in disease rating was partly, if not wholly, due to microbiological antibiosis.   In certain cases this behavior was only temporary.   In this particular experiment, disease expression of the pathogen was, in general, greater and more constant in the natural soil control than in those treated with dextrose or sodium nitrate.   To summarize briefly, these data and additional evidence indicate that one kind of food may have a greater ten-

dency than another to promote the assumed growth of microflora antibiotic to *R. solani*. These results also suggest that the effectiveness of a given nutrient may depend primarily on the initial qualitative growth of microflora which it promotes and not necessarily on its total energy content available for decomposition. Further, the pathogen usually tends to disappear from the soil in cases of frequent or marked disease suppression. Finally, it is recalled that (28) this pathogen may be much more virulent when its vegetative growth is scanty than when it is luxuriant.

TABLE 3

Data indicating variability of virulence of R. solani in successive replantings* of the same soil replicate, and also in different replicates† of the same treatment

TREATMENTS	APPLICATION PER ACRE	pH	REPLICATE NUMBER	AV. DISEASE RATING‡ PER PLANTING							
				1	2	3	4	5	6	7	8
	cwt.			%	%	%	%	%	%	%	%
Sodium nitrate	86	6.2	1	4	0	tr.	tr.	13	3	1	*53*
			2	36	8	5	0	3	tr.	0	*58*
			3	29	11	8	41	50	59	51	60
Sucrose	218	6.2	1	45	43	14	57	54	53	60	60
			2	46	48	62	65	38	60	28	60
			3	1	55	tr.	0	0	54	0	31
Dextrose	218	6.1	1	1	1	tr.	48	60	33	46	27
			2	9	tr.	tr.	46	37	46	14	1
			3	9	0	tr.	tr.	7	0	41	*52*
Controls (natural virgin, black loam, infested)		6.1	1	36	35	52	58	60	60	0	53
			3	52	52	0	60	60	53	60	35
			6	15	7	19	43	49	39	36	10

* 21-day period.

† Italic figures indicate replicate reinoculated after seventh planting.

‡ Based on 10 plants at 16°–17° C., and soil at 30 per cent of moisture-holding capacity.

ROOT ROTS OF WHEAT (*H. sativum*, *F. culmorum*, AND *O. graminis*)

Field experimental evidence relative to the soil sanitation aspect of certain crop rotations on the cereal root-rotting fungi *H. sativum*, *F. culmorum*, and *O. graminis* have been presented by workers for various countries. In general, *H. sativum* and *F. culmorum* are troublesome in a wide variety of soil types, and particularly in old land. They tend to increase rapidly in soil cropped successively to wheat. They are kept within bounds, however, by a crop of oats, certain other crops, and by summer fallow. Since both are strongly saprophytic they soon become well established again. In contrast, *O. graminis* is practically confined to the black loam soils in western Canada, and is also more effectively controlled than the other plant pathogens by a crop of oats, alfalfa, or summer fallow. It becomes re-established very slowly, but much sooner in new than in old land. Since under conditions in western Canada it rarely produces ascospores and is nourished parasitically on spring wheat for only about 75 days, it must live saprophytically or in a resting stage during the remainder of the year.

Though this difference in ability to persist may be partly explained by the fact that *O. graminis* is more highly specialized parasitically than the other two root-rotting fungi, and partly because it may be dependent on certain growth-promoting substances made available by the associated soil fungi and bacteria, and other sources, as suggested by Padwick (20), it is also a fact (25) that this pathogen is, in general, definitely more susceptible than the other two fungi to the antagonistic properties of the associated soil bacteria and fungi.

Broadfoot (2) demonstrated that over a relatively short period of time the inoculum of *O. graminis* was progressively vitiated in a recolonizing, steam-sterilized soil, and this was confirmed later by Ludwig and Henry (18), who recolonized with natural soil. Further, inocula of all three pathogens are most virulent in freshly steam-sterilized soil, whereas in natural soil the disease produced is relatively slight and the inocula soon deteriorate. In striking contrast, inoculum of *R. solani* grown in steam-sterilized soil is least pathogenic in an uncontaminated sterilized soil, fairly virulent in a recolonizing steamed soil, and most virulent in a natural soil (28). The behavior of *A. scabies* (table 1), appears to follow a similar pattern to that of *R. solani*. The reasons for the differences mentioned are not clear.

Garrett (7) considers the biological control of the parasitic phase of *O. graminis* chiefly "growth inhibiting," but its operation on the resting phase "truly fungicidal." He found materials poor or lacking in nitrogen (wheat straw, rye-grass meal, starch) to be most effective in hastening loss of viability of resting mycelium in buried wheat straw, and such materials as dried blood or ammonium carbonate, with a nitrogen content considerably in excess of requirements for complete decomposition, to be ineffective, and even to delay the disappearance of, or protect, the mycelium. Possibly these results would help to explain the successful survival of the pathogen in the wheat stubble of Canadian black loam soils, which are (39) relatively high in nitrogen (0.53 per cent). On the other hand, they do not seem to explain why this fungus is apparently destroyed in the soil of a summer fallow where the combine leaves much straw for decomposition.

For the parasitic phase Garrett (7) says that a high rate of soil respiration checks the growth of the pathogen along the wheat root by increasing (directly and indirectly) the local concentration of carbon dioxide, and suggests periodical organic manuring to stimulate microbial growth, and also a firm seedbed to prevent the diffusion of carbon dioxide.

Fellows (6) obtained control of take-all (*O. graminis*) of wheat under field conditions by the use of chicken manure, alfalfa plant material, and also boiled oats and barley. Tyner (33) found that, under optimum conditions for microbial activity, both *H. sativum* and *F. culmorum* produced appreciable root rot of wheat longer in an artificially infested compost consisting of natural soil and wheat- or barley-straw than did *O. graminis*, and that all three pathogens apparently were less effective in the oat-straw compost, despite practically identical carbohydrate-nitrogen content of the entire compost. He assumed that the bacterial and fungal flora associated with the decomposition of oat straw in his pot cultures was somewhat different from that of the wheat or barley straw.

DISEASE INCIDENCE IN RELATION TO RHIZOSPHERE EFFECT

It has long been observed that a soil infested with a given plant pathogen is restored to health by the growing of certain crops or by cultivation without a crop, and that some of the pathogens tend to disappear more completely than others. A bare summer fallow tends to be as effective as a nonhost crop. This has probably suggested that the reduction of the pathogen was due mainly to the absence of the host. Since it became recognized, however, that certain members of the associated bacterial and fungal flora of the soil might be very antagonistic to, others compatible with, and still others possibly favorable to pathogenic organisms, more attention has been directed toward discovering how certain crops and soil amendments might modify the soil population.

Hiltner (13) defined the term "rhizosphere" as that zone of influence next to the root of the plant, where certain microorganisms were more abundant than in the soil beyond. Subsequently, Starkey (29) and others found that certain kinds of fungi and bacteria were more abundant than others in the rhizosphere. Lochhead *et al.* (17, 37) classified the bacterial population of the rhizosphere and soil into two general groups, one having simple nutritional requirements, and the other more complex ones. The former, which was subdivided into six groups (nos. 1, 2, 3, 4, 6, and 8), was found to be more abundant in the rhizosphere, whereas the latter, which was subdivided into three groups (nos. 5, 6, and 9), was more numerous in the soil beyond the rhizosphere. Thom (30) noted that most of the fungi and bacteria in contact with the root surfaces belonged to species active in the decomposition of fresh organic matter. Lochhead (16) reviewed relevant literature on "rhizosphere effect" and presented additional data. He noted "little or no difference in morphological or physiological groups of bacteria *in soils of different fertility*," but "an unmistakable selective action characteristic of the rhizosphere of all plants studied"—(red clover, mangels, oats, tobacco, corn, flax). As pointed out, "From the standpoint of bacterial physiology the findings indicate a more active bacterial flora in the rhizosphere than in the soil beyond." Timonin (31) reported that a lower water content of the soil tends to increase the density of the bacterial and fungal populations in the rhizosphere, while depressing it in the soil beyond.

The foregoing data seem to suggest a "mechanism" for modifying the microbial balance of the soil, even without the operation of microbial antibiosis. The latter does occur in the soil, and there seems no apparent reason why it would not occur equally well, or better, close to the roots, where, favored by moisture and food, the population is denser and also more varied. The microbial population of both rhizosphere and soil might contribute in various ways to the decrease or the incidence of a soil-borne plant disease. For example, certain fungal or bacterial members may be antibiotic to certain pathogens, thus protecting the roots or other parts attacked; or they might provide bioses for increased growth or virulence of the pathogen to be absorbed by the root, thus increasing the susceptibility of the host; or they might possibly weaken or invade the superficial cells of the host. On the other hand, several possibilities could be suggested with respect to root excretions of host or nonhost plants. For example, in both cases, the population would tend to be both dense and characteristic of

the plant (16); and the excretion might or might not favor the increase of certain fungi or bacteria antibiotic to the pathogen or to other members, some of which possibly provide the pathogen with substances which increase its growth or virulence. Thus, it could be argued that either a host or a nonhost crop might favor the increase or the decrease of a given pathogen. This would depend not only on the nature of the plant secretions but also on the antibiotic and other diverse potentialities of the resulting associated microflora.

Hildebrand and West (12, 38), in a study of the relative effects of various cover crops on the strawberry root-rot disease, showed that the disease was almost completely controlled in a naturally infected root-rot soil in which several crops of soybeans had been incorporated, whereas under a similar treatment with red clover the disease was severe. They emphasized the complex nature of strawberry root rot and pointed out that although representatives of seven genera of fungi and a nematode had been found to be somewhat parasitic to this host, the causal pathogen was still undetermined.

During their studies on the bacterial flora of the rhizosphere of diseased strawberry and healthy cover-crop plants in a root-rot soil, they decided that it was the decomposition of the plant material, and not the living plant, that influenced the bacterial flora *throughout the soil*. The data from soil cultures showed that the decomposition of soybean plant material, glucose, and acetic acid in a strawberry root-rot soil tended to inhibit the development of bacteria belonging to group 3 (simple nutritional needs), but favored a large increase of the bacteria of groups 5, 7, and 9 (complex nutritional requirements), namely, those found in "healthy strawberry soils." Red clover was noted to lack this capacity. Bacterial group 3 was most abundant in the rhizosphere of diseased strawberry plants. The conclusion was that the decomposition of soybean plant material, glucose, and acetic acid in the root-rot soil had reduced disease severity by effecting a marked and favorable modification of the bacterial and fungal flora of the entire soil.

Lochhead (16) concluded that the rhizosphere effect (bacterial) of a variety of flax and a variety of tobacco each susceptible to a different root rot was greater than that of the corresponding resistant variety. He stated, "Although these preliminary findings by no means prove, yet they suggest the possibility, that resistance to a certain disease may be linked up with a selective action of root excretions upon the saprophytic soil microflora, thus favoring types which may be more, and in other cases less, antagonistic (directly or indirectly) towards pathogenic organisms."

From studies on the varieties of flax and tobacco used by Lochhead and on additional resistant and susceptible varieties of tobacco, Timonin (31) concluded that the rhizospheres of susceptible varieties maintained a denser bacterial and fungal population than those of the resistant varieties.

In another study, Timonin (32) concluded that the incidence of *Alternaria*, *Cephalosporium*, *Fusarium*, *Helminthosporium*, and *Verticillium* was relatively lowered in the rhizospheres of Bison flax (resistant to *Fusarium lini*), and that of *Mucor*, *Cladosporium*, *Penicillium*, and *Trichoderma* was increased in the rhizo-

spheres of Novelty, a susceptible variety. The species were not given. Reynolds (22) found that the potential resistance of a variety of flax to *F. lini* is dependent on the linamarin content of the tissue. Timonin (32) showed that *Trichoderma viride* was more tolerant than either *Fusarium* sp. or *Helminthosporium* sp. to minute quantities of hydrocyanic acid. Further experiments should indicate whether the rhizosphere of other susceptible and resistant crop plants show similar differences and possibly the reason.

GENERAL DISCUSSION

In view of the differences in growth response of various soil-inhabiting fungi and bacteria (15, 23, 37) to a number of bioses made available by living plant roots, by decomposing plant material, and by the soil itself, and the impact of such factors as antibiosis and related phenomena, competition, available soil nutrients, temperature, moisture, and soil reaction on the pathogen and other soil microflora, a satisfactory explanation of the development of disease becomes an extremely difficult yet fascinating task. Although any one factor may decide disease incidence, that of nutrition, as related to host, pathogen, and associated microflora, remains basic throughout. Included in this general field is the differential effect that the living roots of different crop plants may exert on the microflora within the rhizosphere and in the soil beyond. If the bacterial or fungal flora of the rhizosphere should be either antagonistic or favorable to the pathogen, its relative importance is increased.

The evidence reviewed in the preceding section, and in tables 1, 2, and 3, indicates possibilities as well as difficulties in disease control by the use of certain plant residues and other soil amendments. More information is required as to why the same amendment may not be equally efficient in reducing disease caused by different pathogens. Also, a study of the nature of the sudden fluctuations in degree of control that often occur during a relatively short time in a given treatment (table 3) might yield significant information.

With respect to disease control by crop sequence, it appears that the pathogen may be more or less constantly confronted with an inhospitable or a favorable "rhizosphere effect," as the case may be, and its growth and persistence affected accordingly. Further critical data on this subject obtained from different crops and different pathogens would be of great academic and practical value.

In disease incidence it is important that the pathogen persist effectively in its soil environment. As the data in tables 2 and 3 indicate, if antibiosis develops, the disease may be reduced or completely suppressed and the pathogen may virtually disappear from the soil within a relatively short time, despite the presence of the host. In fact, *A. scabies* and *R. solani* seem to persist very well without the host. This is probably true also for *H. sativum*, *Fusarium* spp. and certain *Sclerotinia* spp., but not for *O. graminis*, which is more highly specialized parasitically. Nevertheless, the growth of all these pathogens is known to be adversely affected by certain other fungi or bacteria, but not necessarily to the same degree or by the same antagonist. In this connection, Waksman *et al.* have recently shown that in artificial media, many different fungi, actinomycetes

(35), and bacteria (34) manufacture substances of varying degrees of antibiotic activity to other fungi or bacteria. Strain differences exist in this respect. This fact was shown by Sanford and Cormack (27) to be important in the development of root rot of wheat caused by *H. sativum*.

It has not been possible to include in this brief review many valuable contributions related to the various aspects of this paper. Some of the points raised, however, will indicate the complexity of the general problem of biological control of soil-inhabiting plant pathogens, and also the opportunity for further research.

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MICROBIAL ANTAGONISM AND DISEASE CONTROL

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Spectacular success has been achieved in treating certain human diseases with penicillin, which is produced by an antibiotic mold. Predictions have been made that similar phenomenal results are to be expected when microbial antagonism is applied in the control of plant diseases.

It is proposed here to define the present status and the prospects of biological control of plant diseases, as far as it is related to microbial antagonism against soil-borne plant pathogens.[2] The general part is a synopsis of basic concepts of biological control. In the special part emphasis will be upon recent work on two specific pathogens. With regard to other disease-producing organisms, reference is made to previous reviews (3, 4, 10).

APPROACHES AND PRINCIPLES

Approaches

Biological control is dependent upon a favorable microflora in the soil. It is a common observation in pot experiments that certain diseases, such as the root rots of cereals, are more destructive in sterilized than in comparable non-sterilized soil, both being equally inoculated with the pathogens. If bits of the original soil are introduced into the sterilized soil, however, the microflora is quickly reestablished, the pathogen checked, and the disease reduced. Thus the microorganisms of the soil may protect plants against certain soil-borne pathogens or limit their damage.

Two approaches have been employed in exploring possibilities of improving upon nature's biological control: first, inoculation with specific antagonists, and second, provision of more favorable conditions for the antagonistic functions of the existing soil flora.

Soil inoculation with specific organisms. This approach has been suggested and stimulated by achievements in bacterization of legume seed and in introduction of insect parasites. In soil, success of the procedure depends obviously on the predominant development of the antagonistic organisms. Such antagonists have often been reported as strikingly effective in suppressing soil-borne pathogens in sterilized soils. In natural soils, however, results have been mostly negative. Here an abundant soil microflora exists already, whereas sterilized soils provide antagonists with fresh nutrients and freedom from competition, conditions resembling those found in artificial culture media.

Soil modifications favorable for antagonistic organisms. The study of specific antagonistic phenomena in culture media and sterilized soils has led to the perti-

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nent observation that pathogens are most effectively suppressed under conditions favorable for their antagonists. Most of these are saprophytes common in natural soils. Treatments favoring saprophytes in general, or special groups, therefore enhance natural biological control against certain pathogens. This has proved to be true for the control of cotton root rot and of cereal root rots by introducing organic manures, of potato scab by green manuring, and of Rhizoctonia damping-off by acidifying the soil surface layer (2, 5, 7, 11). These practices were known to be beneficial even before their microbiological effect was recognized.

Principles

Natural control. The preceding discussion has shown that biological control of plant pathogens cannot be considered apart from other natural control phenomena. Thompson (9) has presented an illuminating discourse on natural control. Though based on entomological studies, his ideas are applicable to soil-borne pathogens. The principal concepts may be summarized as follows:

The primary factor determining natural control lies in the intrinsic limitations of the specific organisms (parasites) themselves.

Environmental influences which affect parasites and their control are complex and ever-changing. These factors may be separated into biological and physicochemical. The biological environment is subject in turn to the influence of physicochemical conditions.

The biological factors are most important under conditions favorable for life, for example in uniform climates of the tropics. Physical factors are relatively more important in regions unfavorable for life. The part played by biological and physical factors in any given area can be determined only by careful investigation of the specific organism involved.

Biological control. Garrett (4) has emphasized Reinking's useful characterization of two groups of soil-borne pathogens: The "soil invaders," which are unable to compete successfully with other organisms when away from roots, and the "soil inhabitants," which are capable of saprophytic activity in the soil apart from host plants.

The soil invaders as a group have, in Thompson's terms, intrinsic limitations which make them vulnerable to microbial antagonism, primarily during the saprophytic phase of their life cycle. In their parasitic phase they enjoy pure culture conditions in the host tissue, and this head-start gives them an advantage over secondary invaders and strict saprophytes which enter later. The environmental complex which affects these pathogens and their biological control has been summed up by Garrett (4), using manurial control as the typical example:

The continued growing of a particular crop encourages the multiplication of the root-parasites of that crop; the application of organic manure encourages the multiplication of the saprophytic organisms engaging in the various stages of its decomposition. . . . It has been reasonably assumed . . . that this development of the soil saprophytes will check the activity of the plant parasites.

Evidence that this assumption holds true has been presented for organisms of the soil-invader type.

On the other hand, the soil inhabitants which comprise such ubiquitous pathogens as *Rhizoctonia solani* and *Actinomyces scabies* are able to compete rather effectively with the soil population; they are therefore not very susceptible to biological control. It is true that the activities of these pathogens are profoundly influenced by their microbiological environment in the soil (1, 5, 11). But such findings, made under artificial conditions, cannot be applied directly in the field. Indeed, contradictory results have been obtained with some practices which are thought to favor microbial antagonism. In the field, potato scab is usually more severe following applications of stable manure, but the same treatment reduces the disease under certain controlled conditions (5). The role of the microbiological environment, as an integral part of the soil complex affecting the soil-inhabiting pathogens, is little understood at present, and the problem is too complicated to be treated adequately here.

SOIL INVADERS AFFECTED BY MICROBIAL ANTAGONISM[3]

Extensive work on microbial antagonism has been done by students of two pathogenic fungi: *Ophiobolus graminis*, the cause of take-all disease of cereals, and *Phymatotrichum omnivorum*, causing cotton root rot. Ophiobolus is the more specialized parasite of the two. Moreover, it does not produce any structure comparable with the sclerotial resting bodies or the spreading mycelial strands of Phymatotrichum. The saprophytic activities of Ophiobolus are therefore strictly limited to host tissues. When introduced into uncropped soil, the fungus tends to disappear rather rapidly.

Ophiobolus graminis

Agronomic practices and microbial antagonism. The take-all disease of wheat is most destructive in light mineral soils low in organic matter. Many of the practices recommended for its control involve encouragement of antagonistic activities of the saprophytic soil flora. Such measures are: clean fallow, crop rotation, and application of organic manures.

Eradication of Ophiobolus can be accomplished by organic amendments, but only during its saprophytic phase (2, 4). In greenhouse experiments with naturally infested soils, the disease was controlled, even in the parasitic phase, by applying organic manures prior to cropping; however, a second cropping to wheat revealed the persistence of the pathogen. Furthermore, the organic manures could be replaced by inorganic fertilizers supplying sufficient available nitrogen and phosphorus throughout the growth period of the plants (2). On the basis of intensive laboratory experiments, Garrett (4) advanced the hypothesis that during the parasitic phase increased carbon dioxide content of the microclimate of wheat roots is the primary factor in the fungistatic effect of organic manures upon the parasite.

[3] It is the general practice of plant pathologists to use sterilized soils when studying soil-borne pathogens under controlled conditions. Most of the experiments cited here necessitated the use of unsterilized soils.

Environmental conditions. "The most rapid disappearance of Ophiobolus resting mycelium occurred under conditions favoring maximum microbiological activity in the soil" is the conclusion that was reached in laboratory experiments with several soils in which artificially infected wheat straws were incubated for 2–18 weeks (4). Elimination of the fungus was faster in rich and heavy soils than in light ones, and it was hastened in partly sterilized soils and in soils amended with large amounts of organic materials poor in nitrogen. Among the physical factors favorable for elimination were good aeration and soil moisture in the range of 30–80 per cent water-holding capacity. Fluctuating moisture conditions were more beneficial than constant ones, probably because they improved aeration. Ophiobolus was kept viable, however, in air-dry soil or when held at 2–3° C.

In Garrett's experiments, organic amendments rich in nitrogen depressed the biological control of Ophiobolus (4). But this effect was not apparent in Clark's work in which different techniques were used (2). The discrepancy, whether due to differences in temperature of incubation[4] or to other causes, underlines the difficulties encountered in correlating the effects of several variables upon microbial antagonism.

Phymatotrichum omnivorum

Phymatotrichum root rot causes annual losses of about 100–150 million dollars, affecting a variety of crops from Texas to Arizona. Generally applicable, effective control measures have not been found in years of searching, though 3- or 4-year rotations with cereals or certain legumes are beneficial. Sclerotia of the fungus are able to remain viable in the soil for years, even at depths of several feet, posing a formidable obstacle to attempts at eradication. In cotton fields of some sections the disease occurs in circular areas which enlarge for several years and then break up at irregular intervals. In some years, the disease does not recur where plants died early in the previous season. This has been attributed in part to natural biological control.

Biological control in the irrigated Southwest. A successful control method has been developed by King in Arizona (7) on infested land continuously cropped to cotton in alternate treated and untreated ¼-acre plots. In fall or winter, large amounts of organic manures (corral manure, hay, or cut, green field crops) are placed in deep furrows which are then covered with 5–6 inches of soil. One irrigation is applied immediately, and another one shortly before the cotton is planted in beds over the furrows. Every year, during 20 years of experiments, root rot in the treated plots has been considerably less than in the untreated plots. Areas affected with root rot were reduced in one experiment to as low as 1.6 per cent, after 12–14 years of the treatment, against an average of 56 per cent root rot in the untreated plots, and a 2-year test gave 9 and 50 per cent root rot respectively (7). Inorganic fertilizers were ineffective.

King suggests that "the dense population of organisms breaking down the

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[4] Clark's experiments were carried out at "optimum temperature for microbial antagonism," probably at about 30° C.; those of Garrett at 17–22° C.

organic materials, developed a soil condition temporarily unfavorable for the growth and activity of the root rot fungus." Soil samples from manured plots evolved carbon dioxide at a higher rate than samples from the unmanured plots. Direct microscopic observation by means of Cholodny slides revealed Phymatotrichum as the only organism more abundant in unmanured plots, while other fungi and bacteria were most numerous in the manured plots. Evidently in the manured plots, microbiological antagonism reduced the inoculum potential of the pathogen during the most critical period, that is, before the roots penetrate the infested soil. Reduction of inoculum potential was manifested in smaller numbers of dead plants, restriction of affected areas, delayed appearance of disease, and retarded injury to plants—all leading to higher yield per acre. A protective effect was also observed: the manured plots acted as barriers by restricting the advance of Phymatotrichum from adjacent untreated areas.

Microbial antagonism and root-rot control in Texas. The success of the Arizona method has stimulated work toward methods adapted to Texas where cotton is grown without irrigation. The most severe root rot occurs in the heavy blackland soils which were used by Clark, Mitchell, and associates in their researches (2, 8). These studies were focused upon the saprophytic phase, because the microflora of live cotton roots was found to be little affected by organic amendments. The techniques used were suitable for obtaining large uniform lots of sclerotia and quantitative data on their recovery and survival in soils.

Addition of organic amendments to soils kept at optimum moisture and temperature resulted in partial destruction of sclerotia and complete inhibition of mycelial growth from pieces of infected roots. The peak periods of both effects coincided with the period of maximum microbiological activity, which occurred in the first 2–3 weeks following manuring. Decline of the micropopulation permitted growth when Phymatotrichum was subsequently introduced. Destruction* and the rate of elimination of sclerotia were increased by increasing organic materials from 1–5 per cent of the soil mass. Time and mass effects are thus involved.

Organic amendments appeared to stimulate germination of sclerotia in the soil and to lead to their quicker elimination. Observations on stained Cholodny slides suggested the following sequence of events: the germinating sclerotia are colonized by other fungi; then, increasing masses of bacteria and actinomycetes overrun the fungi and sclerotia and eventually decompose them.

Environmental conditions. In lots of soil amended with ground alfalfa tops and kept for 30 days at 2, 12, 28, and 35° C., 12, 30, 72, and 91 per cent of sclerotia were eliminated. In unamended soils destruction of sclerotia at the same temperatures ranged from 27 to 34 per cent. High soil moisture was somewhat better for elimination than low or medium moisture contents in organic-amended but not in unamended soils. Alkaline reaction was most favorable for sclerotial destruction (94–95 per cent at pH 8.0). Elimination fell to 75 per cent at pH 6.5 and to 56 per cent at pH 5.3 but rose again at pH 3.0. This effect of soil reaction was not dependent upon whether original soils were compared or whether one soil was adjusted to a series of pH values.

Better elimination of sclerotia in deep than in shallow containers, whether amended or unamended soils were used, was interpreted as an effect of aeration. The magnitude of the difference varied with the type of amendment, ranging from 4 per cent for wheat straw to 60.6 per cent for stable manure. The complexity of environmental effects thus becomes manifest, as with Ophiobolus, when variations in physical and chemical factors are considered together. In general, organic manures rich in nitrogen were at least as effective as those poor in nitrogen. In shallow containers, however, stable manure was inferior to wheat straw with respect to elimination of sclerotia (2).

Control by early plowing and manuring. Chances of controlling cotton root rot in the field are greatly improved by terminating the parasitic phase early in the season, when soil temperatures are still high enough to make microbial antagonism effective. When cotton roots were cut below the crown in late summer or early fall, the microorganisms of the taproot surfaces increased enormously and remained for 2 months as high as 150–200 times the population of normal root surfaces. Destruction of root-rot mycelium was parallel to this increase. Late cutting was rather ineffective, because low temperature slowed microbial activity.

Logical application of these studies was made in an experiment in a heavily infested field which had been cropped to cotton. Plowing deeply and early in fall, after application of barnyard manure, reduced the dead plants of the next crop to 34 per cent as against 94 per cent in normally bedded plots. The treatment resulted in increased microbial activity, which was carried over to spring, and in destruction of sclerotia above the 12-inch plowsole. Control following early deep plowing alone was not quite so good (8).

BIOLOGICAL CONTROL OF SOIL-BORNE PATHOGENS AND THE MECHANISM OF MICROBIAL ANTAGONISM

Successful control measures which involve microbial antagonism have been developed empirically. Initiation and improvement of such practices would appear to be a joint task for agronomist, soil microbiologist, and pathologist. There is need to consider not only the specific pathogen and its disease relationships, but also its ecological relations within the soil and the adaption of control practices to local climatic and soil conditions affecting the crop.

So far, practical application of biological control has been successful only when using an indirect approach, that is, soil modifications favorable for antagonistic action of the existing microflora. The direct approach, that is, applying specific organisms to soil or seed, has been mainly of theoretical interest. Seed "bacterization," for example, has been proposed by Russian investigators for the control of seed-borne diseases (10), but some chemical treatments are simpler, cheaper, and more effective.

The biological character of disease control by means of incorporating fresh organic manures into soil is apparent in mass and time effects as well as in the influence of favorable physicochemical conditions. It is not a routine practice which is effective in all cases. Rapid increase and maximum activity of the

soil microflora must be brought about at the right period of crop development and climatic conditions.

There is no simple measure by which microbiological factors of environment can be defined in a way comparable to physical factors. Moreover, it is not easy to ascertain the extent to which microbial antagonism is responsible for disease control by organic manures, because they exert nutritional and other effects which are likely to benefit crops without necessarily altering disease resistance. The term "antagonism," originally based on relations between single organisms in pure culture, has been used here to designate the adverse action of a microbiological complex on a pathogen. It might be difficult enough to analyze the factors responsible for the end result if the soil population were static. It is highly dynamic, however, particularly when engaged in decomposition of organic matter. There are successive changes, including shifts in quantitative and qualitative composition of the population, which influence in turn the physicochemical microenvironment. There are synergistic, competitive, parasitic, and toxic activities of one group toward the other. It would appear very difficult, in such complex systems, to evaluate the relative importance of single factors.

Nevertheless, attempts have been made to analyze the mechanism of microbial antagonism in soil. Blair (1) found that the growth of *Rhizoctonia solani* in soil is depressed by addition of wheat straw. He connected this effect with the rapid development of cellulose-decomposing organisms which tend to deprive the Rhizoctonia of nitrogen and further inhibit it through a high rate of carbon dioxide evolution. Another type of analysis has been made with a strawberry root-rot disease, the cause of which is not known. Control of this disease by organic amendments has been connected with the relative abundance of "beneficial" as contrasted with "harmful" bacterial groups in the rhizosphere and the surrounding soil (6). This bacterial "balance-index" is based on quantitative-qualitative analysis of soil populations obtained on nonselective media and separated by groups according to nutritional requirements (12). This work opens a promising approach toward setting up standards for soil microbiological indicators comparable to the phytoindicators used in plant ecology.

The same studies suggest that "the functions of the different species [of the common soil microflora] are exercised most fully under conditions of association." The investigator of microbial antagonism is thus confronted with a dilemma. He cannot understand the complex micropopulation and its activities without analyzing and simplifying. But in doing so, he has to destroy at least to some extent the functional unity which he wants to study.

Fawcett has suggested that synthesis and analysis should go hand in hand, emphasizing the use of known mixtures of organisms in plant-disease investigations (3). With soil-borne diseases, future progress along this line will be made perhaps by means of experimental models made of synthetic soils and "domesticated" antagonists (10). In order to obtain a composite picture of interrelations, techniques are urgently needed which make it feasible to attack complex microbiological problems from several angles. In this way, research may provide the basis for exploiting microbial antagonism through agronomic practices.

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SOIL TEMPERATURE, MOISTURE, AERATION, AND pH AS FACTORS IN DISEASE INCIDENCE

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From the times of Theophrastus (300 B. C.) and Pliny (70 A. D.) to approximately the year 1800 the prevailing agricultural literature was filled with references to unfavorable soil and air conditions as precursors of plant diseases. As late as 1839, Weigmann in his handbook on phytopathology attributed many diseases to cold, sour, wet soil. Von Wildenow (1790) said that climate as well as soil works continual modifications in organisms. In 1795, Plenk noticed that quince trees on high, relatively dry soil remained healthy while the trees planted along a marsh were being killed by some canker.

It would be possible to continue the list of such references for many pages, but it is sufficient to point out that ever since Adam's unwise dabbling in pomology, the environmental influence on plant welfare has been a phenomenon of exceeding interest to man.

Beginning with the early 19th century, the relationship of fungi to disease was so intriguing that ecological relationships, except those discussed in a few textbooks and articles were neglected until about 1900. Since then the literature on the subject has become profuse, and it now is rare that an author presumes to discuss a plant disease and its causal organism without delving into the effects of moisture and temperature. Unfortunately, however, the complex nature of the soil has made investigators more timid in seeking information regarding its temperature and moisture than in studying the same properties of the air.

During this period of transition, from the time when plant disease was believed to be due to environment until it was proved to be caused by a living organism, there were many workers who were intermediate in their thought. They conceded that pathogens were the final cause, but only after unfavorable temperature, moisture, and nutrition had predisposed the plant to disease. Herbert H. Whetzel, in his history of phytopathology, names this group of men the "predispositionists," and lists Paul Sorauer (1837–1916) as the head of the group.

It hardly is possible to determine when the true relations of soil temperature and moisture to disease production were established, but it can be said definitely that in late years, L. R. Jones of Wisconsin and his earlier students had much to do in directing the research pertaining to the influence of the soil on disease in plants. As early as 1912 Jones was lecturing on the subject, especially in connection with cabbage yellows, and a few years later, temperature chambers were devised for studying the reaction of the plant to the organism when temperatures and moistures were raised or lowered.

SOIL TEMPERATURE

Inasmuch as it takes several times as much heat to raise the temperature of moisture-saturated soil as it does that of dry soil, temperature and moisture

cannot be separated completely.   It is known, however, that certain fungi and bacteria thrive when the temperature is high and others when it is relatively low.   Any mycologist, for instance, who has examined collections of leaf spots from the tropics and subtropics and those from the temperate zones, is aware that Cercosporae are far the more numerous in the warmer climates whereas Septoriae predominate where it is cooler.

Among soil organisms, wilt-producing Fusaria have proved to be virulent pathogens as the temperatures rise, at least within certain limits.   As an example may be cited *Fusarium conglutinans*, a soil fungus that causes the yellows of crucifers.   In upper New York State yellows is found commonly on the sandy soils along the Great Lakes and in the Hudson Valley.   Many times, seedlings from this infested area have been transplanted in Cortland County, where the elevation is higher, the rainfall greater, and consequently the soil temperature fairly low.   Almost never is the disease found in the Cortland Valley.

For many years tomato seedlings have been shipped from Georgia to New York State.   Judging from Georgia reports, *Pseudomonas solanacearum*, a wilt-producing organism, should have been present in at least a small percentage of the many thousands of shipments, but the disease has been found in the North only a few times in the last 30 years and then only in the Lower Hudson River Valley or on Long Island.

It is difficult to separate effects of air temperature and those of soil temperature.   Apparently both react in unison.   It has been pointed out by Thompson and Doolittle (10) that Big Vein, a disease of lettuce, is more prevalent and of greater severity during or following low temperatures.   This has been observed in the New York City area when lettuce was set early in the cool soil.   A still better example is oedema, which may be present on greenhouse plants and often affects cabbage leaves after the first cool autumn days.   Whether in the greenhouse or in the field, the soil, containing much moisture, may continue at a high temperature while the air temperature drops sharply.   In consequence, the turgid mesophyll cells become overextended and push apart the lower epidermal cells, through which they protrude.

Many fungi attack the parts of the plant above ground and are not affected directly by soil temperatures.   But in the case of *Phytophthora infestans*, causing late blight of potato, the fungus attacks also the tubers.   This organism is very sensitive to temperature changes, and therefore the soil could well change the temperature of the air immediately above it the few degrees that might mean the difference between infection and noninfection.   When the soil is cold and wet, the air near it could readily drop at night to the 49° to 60°F. range, in which the conidia germinate best.   Then, during the day, when temperatures rise to the 68° to 76° range, infection may take place.

Jones *et al.* (5) recorded interesting data on the effects of soil temperatures on the incidence of disease, using many of our most common soil-inhabiting fungi.   As was expected, the Fusaria which cause wilt of plants invariably produced the disease at high optimum temperatures, 75° to 88° F.   A number of other fungi such as *Thielavia basicola* (black root-rot), *Corticium vagum* (Rhizoc-

tonia), Phthium (root rot of corn), and Aphanomyces (root rot of peas) grew best at 60° to 72° F. or somewhere in that range. It has long been known that onion smut thrives in northern states, where onion seed is planted in cool soil, and can be found in the South only when the crop is grown in the coldest part of the growing season.

Some species of a genus of fungi react differently to the same temperature. *Helminthosporium sativum*, causing a leaf spot of barley, has a high optimum temperature, whereas *H. oryzae*, on rice, has a relatively low one. Dickson (3) pointed out a still more peculiar case. *Giberella saubinetti* attacks both corn and wheat. When the soil in temperature tanks was infested and both corn and wheat were planted in the same containers, there was almost no infection of wheat at 46° F. but this proved to be the optimum temperature for corn infection.

Kunkel (6) has suggested a control of certain virus diseases by heating the plant. He found that in the case of peach yellows if seedlings up to 3.5 feet tall were places in a uniformly heated room at 95° F. for 24 to 27 days, the virus was destroyed and all succeeding growth remained healthy. Peach trees affected with rosette, however, became too susceptible to heat injury to be treated after the virus had once invaded all parts of the plant. In a similar manner, Kunkel (7) destroyed the aster yellows virus in periwinkle by placing the growing plants for 2 weeks in a room heated to 108° F. A somewhat more common control of a virus disease with heat is the case of greenhouse tomatoes infected by spotted wilt. In late winter and early spring, the disease may appear in such a severe form that inexperienced growers consider the possibility of discarding the entire crop. But as soon as the sun heats the greenhouses so that soil and air temperatures rise exceptionally high, the plants gradually recover and show no further symptoms of the disease.

It is not always certain whether the temperature has an effect on the pathogen or whether it influences the susceptibility of the host. It is a common observation that during periods of high temperature in northern states Cercospora celery blight may appear in almost epidemic form. During this time, Septoria blight is absent or much reduced in severity. As soon as cool weather of autumn occurs, Cercospora blight ceases to be a menace, but Septoria blight may develop rapidly. Cercospora, for the most part, is a weak pathogen and possibly it cannot occur on celery in epidemic form until the crop has been weakened by the prevailing high temperatures, especially those of the soil. The relationship of host and pathogen still requires much study.

SOIL MOISTURE AND AERATION

Soil water may be a carrier of pathogens and in this manner help to spread disease. It may be a direct aid in fungus reproduction, as in the case of Phytophthora and Pythium, or it may have a deleterious effect on the host. It has long been observed that when there is an abnormal amount of soil moisture, the wood maturity of stone fruits is delayed in the autumn to such an extent that injury occurs which often is followed by Valsa canker. Strawberry red stele usually is associated with soil that has been saturated for a length of time in-

jurious to the plant. On the other hand, frequent rainfall may keep soil temperatures low and thus reduce the amount of disease caused by organisms favored by high temperatures.

Verticillium, which causes a wilt on many kinds of plants, apparently is unusually sensitive to soil moisture. In one series of greenhouses where the subsoil was impermeable and heavy watering practiced, almost the entire tomato crop was lost because of this wilt. Steam sterilization alone did not seem to help under those conditions. The only remedy was to lay drainage tile deep enough to penetrate this impermeable layer and cover the tile with a layer of finely crushed stone to ensure proper drying of the soil. The same thing holds true on many other crops which are relatively resistant to Verticillium infection. On the other hand, eggplant is very susceptible and will become infected under any condition of watering that will enable the crop to grow well.

Rhizoctonia may cause infection through a wide range of soil moisture. Although infection may be heavier in the more nearly dry soil, it is not always a criterion that Rhizoctonia is affected directly by the moisture content. As an example of this may be cited a pea field on which potatoes had grown the previous season. The farmer only partly leveled the hills where the potato rows had been. Consequently the soil on the ridges was drier than in the intervening furrows. In addition, the pea seed was planted deeper on the ridges, and the plants were several days later in breaking through these than through the intervening soil. This extra time enabled Rhizoctonia to attack the growing tips, with the result that the ridged soil had less than half the stand of the remainder of the field. As proof that Rhizoctonia was not present in unusual amounts in the old potato rows, the peas grew normally wherever the mounds had been leveled uniformly with the remainder of the field.

Clark and Martin (1) of New Jersey found a similar condition in their work on Rhizoctonia of potato. Any condition, whether depth of planting or dryness of soil, which delayed the appearance of the sprout increased Rhizoctonia cankers.

It has been mentioned that Big Vein of lettuce is increased by low temperatures. This might indicate that the disease would be favored by a high moisture content. This has recently been proved by Pryor (8), who found that there was a constantly increasing amount of the disease as the moisture content of the soil rose from 35 per cent of the moisture-holding capacity to 85 per cent.

There has been much debate regarding the effect of soil moisture on the amount of common potato scab. Sanford (9) in 1923 reported that at the lowest range of moisture in which potatoes develop, scab was most abundant. A few other investigators agreed with these findings. More recent workers are inclined to agree with Goss (4) that "while the results are not consistent in repeated tests, there is no evidence that high soil moistures have any depressing effect on the scab organisms." It is probable that since temperature, soil acidity, and moisture all react at the same time on the scab organism, exact duplication of the work of any previous research man is almost impossible. It is not surprising, therefore, that opinions differ. In northeastern United States it generally is considered a fact, at least by growers, that potato scab is more prevalent during dry seasons than during wet ones.

Some pathogens like Plasmodiophora, causing club root of crucifers, have motile spores which swim about in water for a brief period before entering the plant. Such organisms naturally require a high percentage of soil moisture before infection. It has been found in the case of club root that at least 60 per cent of the water-holding capacity for a few days is required for infection, and saturation is even better.

It is possible for relatively dry soil to be packed so hard that air cannot enter and the growing roots suffer from a deficiency of oxygen. The most common lack of aeration, however, is the result of so much free water in the soil that the air is forced out. Well-drained soil almost never lacks in aeration.

SOIL pH

It has been only in recent years that simple methods have been devised for testing the soil alkalinity quickly. Even during this short period, much has been done in the study of soil reaction and the prevalence of disease in plants. Some general observations had been made long before the pH scale came into use. Probably a hundred years ago, it was found in Europe that when the plaster from an old house was spaded under in a garden, club root of cabbage was controlled. When early settlers in northeastern United States burned logs and later planted potatoes, they found that at times the tubers in the areas where the ash piles had been were exceedingly scabby. On some farms this effect was noticeable for at least fifty years after the clearing had been made.

At present it is known that many pathogens are sensitive to soil reaction. For instance, Crawford (2) remarks that *Phymatotrichum omnivorum* root rot is endemic in certain parts of the Southwest where the soil is alkaline. Kirby, when making a survey of take-all of wheat in New York State, found that during the seasons when the disease was prevalent, it could be found regularly in the high-lime areas but was almost entirely absent beyond the border of these specific areas. Several authors have asserted that *Pseudomonas solanacearum* causes most injury in acid soils, although Davidson, working in Ceylon, refutes the statement by saying, "Locally the disease appears to be more severe on alkaline than on acid soils." Here again, it may be that several factors are equally concerned, so that opposing results may be reported.

Probably no single soil factor works without being influenced by other factors. As an illustration of this may be mentioned club root of crucifers. Work done by the writer in New Jersey and later verified in New York showed that the club root pathogen was almost completely controlled when the soil pH was raised to 7.2. This was demonstrated so often in New York State that few commercial cabbage or cauliflower growers fail to have their soil tested, and if club root has been present, add the required amount of hydrated lime. Walker of Wisconsin, in conversation, says that even though this practice may be an excellent control measure under eastern conditions, it has not proved nearly so effective under the dry soil conditions of his state.

The various species of Actinomyces causing scab on potatoes and root crops are interesting in that they react differently at different degrees of soil acidity. Rare species may grow in a soil with a reaction of pH 4.2. Most species, how-

ever, begin marked activity only at pH 5.0 or higher. Above pH 7.0 their activity is much decreased, permitting almost scab-free potatoes at pH 8.0. This degree of alkalinity often is reached in the high-lime areas.

According to the work of Buchholtz in Iowa, Pythium damping-off of sugar beet and of alfalfa is reduced by adding lime to the soil.

The manipulation of soil reaction for controlling disease has not been put into practice as often as might seem advisable. This lack is due in part to the effect the change might have on succeeding crops. It has been observed by Haenseler and others that heavy applications of sulfur, which produce an acid condition in the soil, will reduce Verticillium wilt of eggplant. But the residual effect of the sulfur on the crops that follow may be most deleterious. For this reason sulfur rarely is used. Occasionally potato growers may apply a few hundred pounds an acre to reduce scab. They make these applications with the greatest caution in order that future yields may not be reduced. Small changes in soil reaction can be accomplished most easily and with least fear of ill effects by applying liberal amounts of sulfate of ammonia, year after year, until the desired soil acidity is attained.

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PATHOGENIC AND PHYSIOGENIC DAMPING-OFF[1]

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Pathogenic damping-off involves decay and disintegration of seedling stems, particularly at or near the surface of the soil. In early stages, water-soaking, discoloration, and collapse of cortical tissues along this part of the stem are evident. Scattered lesions on roots may occur. The plants finally topple over, or the stems break readily from the roots (fig. 1).

A striking feature of pathogenic damping-off is often the rapidity of its progress; seedlings seemingly healthy one day may show advanced stages of disease a day or two later. This is especially the case when damp soil, humid air, dull light, and warmth combine to produce soft plant tissues and great fungus activity. Spread to healthy plants is rapid from the first plants attacked, the limits of disease advancing 1 or 2 inches in 24 hours. With prolonged dampness, the fine thread-like mycelium of the parasite overgrowing the fallen plants becomes discernible. These may undergo complete decomposition with scant remnants to indicate that the area of soil had been occupied. On the other hand, it is not unusual for a change to bright light and drying conditions to check abruptly the progress of disease.

Pathogenic damping-off can destroy plants during germination before emergence from the soil. Damage can be just as severe during this pre-emergence period as during the postemergence period just described. Weak seedlings, or those from old seed which germinate slowly, are more likely to succumb at this time. When conditions for germination are particularly unfavorable, such as soil too cold or too wet, even seedlings from highly viable seed may fail to emerge, or germination may progress little beyond imbibition and the loss consist mostly of seed decay.

The name "damping-off" indicates that early plant growers considered excess moisture the primary cause of trouble. The first evidence of the causal relation of fungi appears to have been suggested by Hesse's description of *Pythium debaryanum* as a parasite of several kinds of seedling plants in Germany in 1874. In American literature, the first definite account of the disease and the problem it offers the grower of seedlings was given by Atkinson (1) in 1895.

Physiogenic damping-off comprises injuries caused by physical or nonliving factors of the environment. These injuries may be termed "noninfectious or nonparasitic diseases" because no causal organisms are essential for their development. The symptoms of physiogenic damping-off are often very similar

to those of pathogenic damping-off, although the similarity has not always been noted in the literature.

A physiogenic disease which is very similar to pathogenic damping-off is "burning-off" or heat canker. Young stem tissues near the ground level may be critically injured by high temperature and excessive drying of the soil, particularly if the latter has become encrusted about the plants as a result of preceding rainfall. Moisture may be actually extracted from tender tissues so that they collapse and the seedlings topple over and die. This trouble is comparatively common with seedlings of parsley, carrots, flax, and some deciduous and conifer-
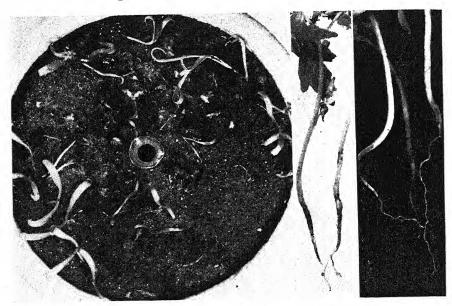
Fig. 1. Typical Symptoms of Damping-Off

Left, a jar of infested soil, in which 150 spinach seeds were planted, showing 40 emerged seedlings of which all but 8 have damped-off; middle, lesions on tomato seedlings caused by *Rhizoctonia solani;* right, lesions on tomato seedlings caused by *Pythium ultimum.*

ous trees. Serious loss of stand may result. In the case of the heat canker of flax, the critical temperature for injury is about 54° C.

Comparable injury to seedlings may result from too great concentration of the soil solutes. The evaporation of moisture may accumulate injurious amounts of salts in the topsoil or leave deposits of them on the surface and about the stems of plants. The osmotic action of these salts removes water from plant cells and causes plasmolysis and the ultimate death of tissues. Since stem tissues near the ground level are most severely affected, symptoms may resemble pathogenic damping-off so closely that microscopic examination is necessary to show that damping-off organisms are absent and not the cause of the disease. Such injury is often serious in alkali soils, but it may occur also in sand culture if nutrient salts are too heavily applied. Damage is increased by high temperature or may be caused by the joint action of excess salts and high temperature.

An excess of soluble matter in soil may be evidenced by retarded plant growth, the scarcity or death of root hairs and rootlets, and the general restriction of the root system. It may be evidenced merely by the inhibition or delay of seed germination. New data concerning effects upon germination have been given by Dunkle and Merkle (7), who point out that excess soluble matter is a common trouble following liberal fertilization or steam treatment of soils in greenhouses and seedbeds. Excess salts may be washed from the soil, provided the beds are raised or underlaid with tile.

Ammonia is commonly a toxic substance in soil for a variable period after steam treatment. If the soil contains much nitrate or fresh organic matter, or if the steam treatment has been lengthy, enough ammonia may be produced to injure rootlets and retard plant growth for as long as a month. Other chemicals occasionally and inadvertently applied to soil may prove toxic to plants.

In frequent cases, the death of roots is caused by water-logging and the exclusion of air from the soil, especially if this condition continues any considerable length of time. Chilling may damage exterior tissues without killing the whole plant.

These different physiogenic injuries are often closely associated with damping-off organisms because damaged tissues provide suitable openings for the subsequent entrance of these parasites. In general, unfavorable environmental factors play important roles in predisposing seedlings to attack by damping-off organisms even though the primary effects of such factors may not be great enough to produce discernible injury or death. Any departure from optimum conditions for growth of the host may so operate as to give the parasite ascendancy. In subsequent sections, some examples of the effects of environmental factors will be discussed further, including those of high temperature and the concentration of solutes. It is often difficult, however, to separate the effects of different factors.

THE PATHOGENIC DISEASE

Plants affected

Most species of plants are susceptible in some degree to damping-off.[3] The seedlings of certain plants, however, are notably subject to the disease on account of natural succulence; examples are spinach, beets, cress, cucumbers, peas, zinnia, and sunflower. Others are very liable to attack because their seeds are inherently slow to germinate; among such are forest tree seedlings, particularly the conifers.

Plant cuttings are subject to heavy loss because wounding lays susceptible tissues open to easy invasion by parasitic fungi until callousing again forms a natural barrier and rooting permits normal growth and resistance. Seedlings requiring transplanting, such as tomato, pepper, eggplant, and various annual flowers, may suffer great loss because the usual thick sowing facilitates the

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[3] Hereafter in this paper the word *damping-off* will be used to signify the pathogenic disease unless otherwise qualified.

spread of the parasites in the seedbeds. The wounding incident to transplanting also provides a period for easy invasion. Such operations are commonly carried out in winter or early spring when long periods of damp weather are likely to occur and favor infection.

As a rule, seedlings are also more susceptible to physiogenic damping-off than are older plants.

Importance

Among the plant diseases associated with soil, damping-off is probably the most common, widespread, and important. Virtually all tilled soil is infested to a greater or less degree with some of the several causal organisms. Under usual cultural conditions, there is significant but often unperceived loss caused by seed decay, failure of weak seedlings to emerge, and retarded growth, all resulting from the attack of damping-off fungi. Extensive loss of stand may make replanting necessary, but additional seed may be unobtainable, or the delay in the crop may lose the best market. Intensive culture of plants, particularly under glass or other cover, cannot be practiced long before increasing soil infestation leads to recurrent disastrous loss, unless routine control measures are undertaken.

Causal organisms

Damping-off may be caused by a variety of parasitic fungi inhabiting the soil. Foremost as causal organisms are *Pythium* spp., *Corticium vagum* B. and C., and *Fusarium* spp. in the order of their probable importance. Some other genera having members known to cause damping-off are *Aphanomyces*, *Phytophthora*, *Sclerotinia*, *Botrytis*, *Sclerotium*, *Thielavia*, *Colletotrichum*, *Gloeosporium*, and *Phoma*. In general, species of these genera cause serious plant diseases beyong the seedling stage as well. Certain bacteria and many additional fungi may be involved in seed decay.

For a time after Hesse described *Pythium debaryanum*, any *Pythium* found to cause the disease was assigned to this species, but in 1927 Drechsler (6) reported that *P. ultimum* Trow. is the species most often met in damping-off, stem rot, and root injury, although *P. debaryanum* is fairly common. A few other species of *Pythium* are reported to cause damping-off or similar injury. *P. irregulare* Buisman on red pine (9) is worthy of mention.

The mycelium of *Pythium* grows rapidly, and upon a rich medium such as steamed rye soon develops a white cottony aerial growth. It branches irregularly and lacks cross walls except for the spore-bearing stalks and old hyphae. Two kinds of spores, conidia with thin walls and oospores with thick walls, are produced. Both are spherical and can be seen with the microscope within invaded tissues. The conidia may germinate in a short time and function largely in dissemination. The oospores are more important in enabling the parasite to survive winter or dry periods, which apparently can be considerably longer than the usual intervals between affected crops.

The mycelium grows between and within cells of the host. Research by Butler (5) indicates that enzyme action may aid in the penetration of cell walls by hyphal tips. Hawkins and Harvey (8) show that differences in varietal resistance of potato tubers to invasion by *P. debaryanum* is correlated with the resistance of their cell walls to mechanical puncture. As cell walls acquire secondary thickening, or become cutinized or suberized, resistance to invasion increases. As a rule, young plants attain a high degree of resistance to *Pythium* when 10 to 15 days old, unless wounding again exposes susceptible tissues. Beach and Chen (2) observed that tomato seedlings after being transplanted passed through a period of susceptibility lasting about 3 days. This early acquirement of resistance by host plants tends to make *Pythium* essentially a parasite of seedlings.

Corticium vagum B. and C. usually occurs as a sterile mycelium and is known in this state as *Rhizoctonia solani* Kuhn. It is a vigorous parasite and attacks a great variety of plants at all stages of growth. The mycelium is but little less rapid in growth than *Pythium* and occurs between and within host cells. Upon stems and roots, extensive lesions, usually dark in color, are produced, and many plants are ultimately killed. As a dormant stage, the fungus forms brownish-black bodies of firm texture called "sclerotia." These are irregular in shape and vary from 1 to more than 15 mm. in breadth. They can often be observed on the surface of lesions and remain viable for long periods under dry conditions. When *Rhizoctonia* predominates in beds of seedlings, surviving plants continue to exhibit varying degrees of injury and retardation of growth.

Little effort has been made to distinguish the species of *Fusarium* that may be concerned in damping-off and seed decay. Species causing wilts in later stages of plant growth can doubtless attack in the seedling stage. But many additional species are likely involved in seed decay. Species of *Fusarium* produce spores prolifically. One type, the chlamydospore, has thick walls, which enable these fungi to survive adverse conditions for long periods, probably several years. Wounding is important for invasion of plant tissues by species of *Fusarium*.

These fungi which are most important in damping-off do not depend altogether on parasitism for sustenance. They are facultative parasites and can live on dead plant materials, including humus, which is an essential part of a fertile soil. Frequently when a seedbed has been damp prior to seeding, mycelium of one or more of the fungi has already ramified profusely in the surface soil and can attack sprouting seed immediately and severely. In this manner, weak parasites are able to do harm

Relative prevalence

Although damping-off organisms are widely distributed in cultivated soils, their relative prevalence, or the damage each does at a particular time or place, fluctuates widely through the interaction of environmental factors. This is indicated by the data in table 1, which records the percentage of colonies of *Pythium, Rhizoctonia, Fusarium,* and various molds obtained from stem lesions of diseased seedlings. These were grown at different seasons with the use of a

similar soil mixture in the greenhouse at The Pennsylvania State College. *Pythium* tends to predominate during cold months, while *Rhizoctonia* and *Fusarium* tend to predominate during warm months. The predominance of *Pythium* under glass in winter or early spring is also indicated by reports of other workers. The various molds represented 12 genera, and no relation to season is indicated.

TABLE 1

Percentage of colonies of the chief damping-off fungi obtained from stem lesions on seedlings at different seasons

MONTH	KIND OF SEEDLING	NUMBER OF STEMS	PERCENTAGE OF COLONIES				
			Py-thium	Rhizoc-tonia	Fusar-ium	Various molds	Sterile
Jan.....................	Spinach	100	47	11	10	19	13
Feb.....................	Spinach	150	28	7	7	47	11
Feb.....................	Peas	100	48	0	12	40	0
Feb.....................	Tomato	200	83	2	8	7	0
May....................	Tomato	200	6	5	44	40	5
June..................	Beets	120	3	33	31	9	24
July...................	Spinach	300	5	26	23	35	11
Nov...................	Spinach	150	11	22	33	11	23

* Infected stems were laid on cornmeal agar of pH 5.5 after mild surface disinfection with sodium hypochlorite and washing in sterile water. Various molds were noted only when the other fungi were absent.

EFFECTS OF ENVIRONMENTAL FACTORS ON DAMPING-OFF

Temperature

Pythium and *Rhizoctonia* have cardinal temperatures for growth which do not differ greatly; respectively, the minima are 5° and 9°, optima between 27° and 30°, and maxima 40° and 33° C. These parasites can cause serious disease over the wide range of 15° to 30° C., a range to which the growth of most host plants is also well adapted. *Fusarium* spp. are generally most active between 25° and 30° C.

A case in which a difference in temperature relationship between host and parasite has importance is reported by Buckholtz (4) in his study of factors influencing the pathogenicity of *P. debaryanum* on sugar-beet seedlings. He found that soil temperatures of 15° C. and below were less favorable to damping-off than to germination and emergence of seedlings. This supported the experience of growers that early spring sowing in Iowa gave best stands. Indirectly, temperatures of 30° and above can also check *Pythium*, particularly when they hasten the drying of the soil by more rapid evaporation. Through low temperatures, or from 10° to 16° C., it is possible to reduce greatly the attack of carnations by *Rhizoctonia*.

In the transplanting of tomato seedlings into infested soil, Beach and Chen (2) found that temperatures below 15° or above 30° C. retarded the host more than the parasites and apparently predisposed the former to damping-off. When

losses of 50 per cent and greater occurred in flats on the open bench of the greenhouse, it was noteworthy that transplanting was accompanied either by temperatures above 30° for the immediate day or by temperatures below 15° for several days. With either temperature extreme, normal growth of the seedlings, especially the putting forth of new roots, was checked, and the plants fell victims to damping-off.

In the development of the physiogenic disease "burning-off," soil temperature has arisen to 40° C. and above, or has tended to be beyond the range of growth for both host and parasite.

Light

Although direct sunlight usually tends to check plant diseases, the exposure of recently transplanted seedlings to it for even a few hours results in a great increase of susceptibility to damping-off. High susceptibility appears to result from the pronounced wilting and the consequent interruption of growth.

Moisture

Damping-off can be severe when the soil holds just enough moisture for good plant growth, or about 50 per cent of saturation. In general, increasing moisture above 50 per cent gives progressively poorer stands of most kinds of seedlings in untreated soil. Injury to plants, however, may become more physiogenic than otherwise as moisture nears saturation. *Pythium* can cause appreciable damping-off when moisture is too low for the uniform germination of many kinds of seeds. Roth and Riker (9) have reported that damping-off by *P. irregulare* is incipient when moisture is somewhat below 20 per cent and that the percentage of disease shows a continuous increase with the rise of moisture until saturation is reached. These workers as well as Blair (3) have shown that *Rhizoctonia* can grow in fairly dry soil; that the progress of the parasite is rapid at one third of saturation but declines sharply as two thirds is exceeded.

Pythium is sensitive to drying of the surface soil. To assure a loss experimentally as high as 50 per cent in transplanted tomato seedlings with temperature near the optimum, Beach and Chen (2) found it necessary to infest the surface soil with fresh mycelium and use moist chambers. If flats of soil thus infested were exposed to drying for a day on the open bench before transplanting, the effect of the mycelial infestation declined decidedly, and loss scarcely exceeded the 3 to 15 per cent experienced with ordinary untreated soil. It is probable that *Rhizoctonia* displaced *Pythium* during the warm months (table 1) because longer periods of light and higher temperature dried the soil frequently and interrupted the development of the latter fungus.

When soil intended for flats or potting is kept air-dry for a week before use, stands of seedlings are markedly increased in comparison with soil kept with moisture at 35 per cent or more of capacity for a like period. Differences in stand in excess of 50 per cent have been obtained in this manner with spinach, cucumbers, and sweet corn. Corresponding differences have been obtained with transplanted pepper and tomato seedlings. Apparently damping-off fungi in

the dried soil are unable to develop sufficient mycelial growth for vigorous attack before seeds are well advanced in germination or before transplanted seedlings have renewed growth.

Soil acidity

The fungi most concerned in damping-off are adapted to a pH range wider than that of most cultivated plants, or from below 4 up to 9. If the pH of the soil is optimum for a particular crop, it is better able to resist or escape attack, probably because the seeds germinate faster and more uniformly. Buckholtz (4) has reported a correlation of 0.745 between soil pH below 6.5 and poor stands of sugar-beet seedlings caused by *P. debaryanum*. In experiments with spinach, beets, and tomatoes in untreated soil at The Pennsylvania State College, damping-off tended to be twice to thrice greater below pH 6.5 than throughout the range above this level. In contrast, Roth and Riker (9) have reported a broad range very favorable for the attack of red pine seedlings by *P. irregulare* extending from about pH 5.2 to beyond 8.5, while below pH 5.2 the percentage of disease fell rapidly. *Rhizoctonia* attacked this host moderately between pH 5.2 and 7.8, but more severely below pH 5.2. These differences in the severity of attack seem to be explained largely by the position of the host optimum, which is pH 5.2 for red pine but near 6.5 for the other mentioned plants.

Humus

The ability of damping-off fungi to grow upon humus imposes a special danger when soil has been treated by steam or other means of disinfection. The destruction of competing organisms and the release of considerable readily available food by the treatment often enables these fungi to spread more rapidly than in untreated soil. It is essential to avoid recontamination of treated soil by these organisms. An important object in the use of washed sand and nutrient salts as a seedbed is to obtain a medium free of organic matter so that fungi can not spread readily from plant to plant.

Concentration of solutes

The likelihood of chemical injury to seedlings by too great concentration of soluble matter depends upon how low the moisture content of the soil becomes as well as upon temperature. Dunkle and Merkle (7) have tentatively placed the "ceiling" value of soluble matter for safe culture of the more sensitive crops like tomato at 0.4 per cent of the dry weight of soils. The "ceiling" value is much lower in pure sand, since buffer substances are largely absent. In experiments by Beach and Chen (2), chemical injury to tomato seedlings occurred in quartz sand when the nutrient salts represented but 0.18 per cent of its dry weight. This was equivalent to 7500 p.p.m. of capillary moisture when the sand held its full capacity of 24 per cent. Safe culture required somewhat less than this amount of soluble matter. Ample food for seedlings will be supplied if the proportion of nutrient salts does not exceed 0.04 per cent of the dry weight of the sand.

Damping-off fungi apparently tolerate or survive concentrations of salts which seriously injure rootlets or "burn" the stems of seedlings during high temperature and drying. Injured seedlings show great ability to recover if damping-off fungi are not present to invade destroyed tissues when moisture is replenished. It is advisable to rewash sand in hot water after each seedling crop, otherwise damping-off fungi may be carried over to the next crop in old roots and dead seed, and injurious concentrations of soluble matter may be built up by succeeding applications of nutrients. Both *Pythium* and *Rhizoctonia* have been observed attacking after physiogenic injury has occurred in commercial greenhouses.

CONTROL OF DAMPING-OFF

The treatment of seeds with a fungicide is the chief method of controlling damping-off when sowing is made in untreated soil. It is particularly important to apply a dust fungicide to seeds after they receive hot-water treatment designed to kill certain internal parasites, for the previous soaking makes seeds very susceptible to attack by soil organisms. A fungicide on seed coats gives seedlings a great measure of protection throughout germination. After emergence, the period of protection can be extended by applying fungicides as drenches, especially in seedbeds.

The actual benefits accruing from seed treatments depend much upon the various environmental factors attending germination. Countrywide cooperative tests of the dust fungicides by plant pathologists using different crops have resulted in significantly better stands in the majority of cases. The lack of a significant difference between stands of seedlings from treated and untreated seeds is due largely to conditions which favor good germination of both.

Highly efficient control of damping-off requires soil treatment as well as seed treatment. Several different methods may be used to destroy parasitic fungi in soil, including heating by steam, hot water, or electricity and the application of various chemical disinfectants. Soil treatment plus seed treatment usually results in seedlings essentially free of disease. Both treatments are advisable when seedlings are to be transplanted. Sand culture is also effective in the production of healthy seedlings. According to tests by Stoutemyer, Close and Hope (10), shredded sphagnum moss provides a seeding medium which effectually prevents the development of damping-off. The very acid reaction of sphagnum may be factor in the prevention of the disease, but does not wholly explain it. Use of this material offers a simple method for the growth of healthy seedlings by home gardeners and small-scale commercial growers.

Healthy seedlings grown according to the previously mentioned methods may give reductions of as much as 50 per cent in damping-off following transplanting in comparison with seedlings from untreated soil. If the transplanting soil gives evidence of considerable infestation, this soil also should be treated.

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SOIL MANAGEMENT AND PLANT NUTRITION IN RELATION TO DISEASE DEVELOPMENT

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In many researches in the past, the relation of the nutrition of the host plant to the development of diseases incited by parasitic microorganisms has been studied. Interesting effects of various major elements, particularly nitrogen, phosphorus, and potassium, have been found. A comprehensive recent review of the subject by Wingard (23) will acquaint the reader with many of the important papers. It goes without saying that the relation of various pathogens and their hosts represents such a wide range of interactions that no simple physiological pattern can be expected. Likewise, it is apparent that no simple relation between the health of the plant and its nutrition can be anticipated. It is true that the cases of apparent or real increase in susceptibility to disease resulting from high nitrogen fertilization are more numerous than those to the contrary, whereas with phosphorus and potassium the reverse is the case. Nevertheless, tendencies in the opposite direction for each element are not difficult to find. What we have so far is, in a large measure, an indication that plant nutrition is one of the environal factors which, along with others such as temperature, humidity, soil moisture, and soil reaction, may have a measurable effect upon the course of disease development. What we need is more intensive research both under controlled nutrient culture and in the field with specific hosts and their parasites before we may expect to have a basis for generalization.

FUSARIUM WILT DISEASES

There is a group of closely related diseases of herbaceous plants, known as the "*Fusarium* wilts," which is of particular interest in this connection, since the pathogens concerned are all bona fide members of the soil flora. They all belong to a group within the large genus *Fusarium* and differ from other members of this genus in that they become parasitic by gaining access to the vascular system of the plant, usually through the fibrous root system, and by bringing about the disease reaction through their habitation within the larger vessels. Generally, they subsist indefinitely in soil to which they are adapted, a fact which may be taken to imply that they exist as free-living fungi in competition with other soil organisms. In this respect they differ from many plant pathogens which seem to have little or no competitive properties and disappear fairly promptly in the absence of the host or with the disintegration of infected host refuse. Though the vascular *Fusaria* have the capacity to live indefinitely as saprophytes and are among the most easily cultured on artificial media, they resemble in parasitic habit such obligate parasites as the rusts in that they are restricted in their selective pathogenicity usually to a single species of higher plants and commonly to varieties, strains, or individuals within that species.

It is a matter of considerable interest to those concerned with the study of soil nutrition that several of these wilt diseases have been shown to be retarded

by an increase in the potassium complement in the soil nutrient. Only recently Stoddard (17) reported a reduction in F. *oxysporum* f. *melonis* (L. & C.) S. & H. in Maryland through the use of a high ratio of potassium to nitrogen in the fertilizer. The most interesting case, however, is that of cotton [F. *oxysporum* f. *vasinfectum* (Atk.) S. & H.]. Neal (11) pointed out in 1927 that potassium salts reduced wilt in sand cultures, and he obtained comparable results in the field in Mississippi.

Walker (21) applied fertilizers of several formulas, including one or more relatively high in potassium, to soil infested with the cotton-wilt organism in Florida, without obtaining any reduction in the percentage of diseased plants. Miles (9) pointed out that Walker's wilt counts were very high (58 to 90 per cent) and that the potassium content of the soil before the applications were made were not reported. Continuing field experiments over a period of years in Mississippi on potassium-deficient soils, Miles (9) obtained rather consistent reduction of wilt with potash fertilizers. Where a very susceptible variety of cotton was used, however, the reduction of wilt was not enough to constitute satisfactory control. On the other hand, in one series of experiments the variety used was very resistant and the percentage of disease was so low that nutritional effects could not be measured. Extensive field experiments in Arkansas also showed that potash fertilizers applied to potassium-deficient soils reduced the incidence of wilt. Young and Tharp (24) studied the effect of various formulas on Half and Half, the susceptible variety used by Miles; on Rowden 2088, a moderately resistant variety; and on Cook, a highly resistant variety. When 0–8–0 and 6–8–0 were used, there was usually an increase in wilt, whereas when potassium was included, wilt was reduced. As in the Mississippi experiments, the wilt in the susceptible variety was not reduced to a negligible factor. It was obvious that fertilizer treatment must be combined with inherent resistance in the variety used to attain adequate control on heavily infested soil.

Cabbage yellows [*Fusarium oxysporum* f. *conglutinans* (Wr.) S. & H.], another vascular *Fusarium* disease, has been studied critically in this laboratory from the standpoint of environal relations, nutritional effects, and inherited host resistance. Two types of inherited host resistance have been defined. One of these (type B) is controlled by the interaction of an undetermined number of genes. Complete immunity is not attained, and a variable percentage of very susceptible individuals occurs in each generation. Furthermore, with increase in soil temperature the percentage of diseased individuals increases, and resistance is gradually broken down. This type of resistance is present in the Wisconsin Hollander, Bugner, and Wisconsin All Seasons varieties. The second type of resistance (type A) amounts to almost complete immunity except at extremely high constant soil temperatures produced experimentally. Since it is controlled by a single dominant gene, fixed homozygous resistant lines can be secured and maintained indefinitely under proper controls. Jersey Queen, Marion Market, and Wisconsin Ballhead varieties carry this type of resistance. Penn State Ballhead and an uncommon variety known as Smith's Pride are virtually devoid of genes for either type of resistance. For the purposes of this study, Wisconsin

Ballhead, Wisconsin Hollander, and Smith's Pride were chosen as representative of type A resistance, type B resistance, and extreme susceptibility, respectively. Since the details of the investigation have been published elsewhere (19, 20), it will suffice to summarize the results here

With the use of the constant-drip sand-culture technique and Hoagland's balanced solution as the basal nutrient, salt concentration and ion balance were varied and series were run near the optimum temperature for the disease (25°C.) and also at the suboptimum level (19°C.) that was somewhat more in line with prevailing field conditions in the upper corn belt.

With concentrations of $\frac{1}{10}$ basal, $\frac{1}{2}$ basal, basal, 2 times basal, and 3 times basal, there was, except in some cases at the two lowest levels, a progressive decrease in rate of disease development up to and including 3 times basal. In the susceptible variety, the differences were most striking at 19°C., under which environment disease progress was retarded by temperature. At 25°, where disease progress was increased markedly by temperature, the same relation of nutrient level to inhibition of disease was evident, but the differences between the various nutrient levels were much smaller. With the type B resistant variety the host was sufficiently resistant at 19° to preclude any measurable difference in disease progress at the various nutrient levels. At 25°, however, inherent resistance was prevented from expression to the extent that the disease progressed at about the same rate as in the susceptible variety at 19°. With such an environal setting, the inhibition of disease progress with the increase in nutrient concentration was expressed in the same manner and essentially to the same degree as in the susceptible variety at 19°.

The type A resistant variety was in extreme contrast with the susceptible and the type B resistant varieties in that it remained completely free from signs of disease at both 19° and 25°C. and at every nutrient level.

The relative influence of nitrate, phosphate, and potassium ions upon disease development was studied by growing the plants at a given nutrient level with a balanced solution for a time and then omitting or increasing the ion concerned. In general, decrease in the potassium ion increased disease progress, whereas decrease in phosphate or nitrate ions decreased disease progress. Again the differences in the susceptible variety were greater at the lower temperature. They were obscured by the lower temperature in the type B variety, but they assumed the same pattern in this variety at 25° C. as in the susceptible variety at 19°. The type A resistant variety again remained free from disease at every ion balance and at each temperature.

This study presented the opportunity to evaluate the interaction of three distinct factors, two of them environal and one genetic, upon the expression of host resistance and disease development. When the resistance of the host was of type A (Wisconsin Ballhead), it was so complete that the influence of the temperature and of nutrition was no longer expressed. When an intermediate level of resistance (type B) was present in the host (Wisconsin Hollander) the interaction of the secondary factors, temperature and nutrition, became evident. At 19°C., type B resistance and temperature, working together, prevented the

expression of any measurable reaction to nutrition, whereas at 25°, where the repressive influence of temperature was removed, the influence of nutrition became evident. When inherent resistance was lacking in the host (Smith's Pride), the interaction of the two environal factors was more clearly expressed. At 19°, where temperature retarded disease development by slowing down action of the parasite, the interaction of the nutrient was very evident. At 25°, where temperature had no restraining influence upon disease progress, the influence of nutrition alone on disease development, although measurable, was least pronounced. It is indicated, therefore, that temperature and inherent host resistance are more important than host nutrition in their influence upon the development of cabbage yellows.

Schroeder and Walker (14) studied the relation of host nutrition to the development of Fusarium wilt [*F. oxysporum* f. *pisi* (Lindf.) race 1 S. &. H.] of garden pea. A resistant and a susceptible variety were grown in inoculated quartz sand maintained at 21° C., which was near the optimum for the host and 6° below the optimum for the parasite. There was no effect of nutrient concentration on disease development during short midwinter days with low light intensity. In longer days with higher light intensity there was a decrease in wilt development with increase in nutrient concentration. This was more marked in the susceptible than in the resistant variety. When the study was conducted at 27°, which was optimum for the pathogen and very unfavorable to the host, a condition not ordinarily associated with this disease in nature became prominent. This consisted of cortical decay of the roots. At this temperature the response of the combined effect of the two phases of the disease was quite different from the response to wilt at 21°. In short days there was an increase in cortical necrosis with increase in nutrient concentration, whereas in long days the disease declined from the lowest concentration to the next higher concentration but increased markedly with two still higher concentrations. It was obvious that the two distinct phases of the disease responded differently to nutrient concentration.

Other work in progress with Fusarium wilt [*F. oxysporum* f. *lycopersici* (Sacc.) S. & H.] of tomato shows the same general type of response of the disease to variation in nutrient concentration and ion balance reported for cabbage yellows.

REACTION OF TWO DISTINCT TYPES OF DISEASE TO NUTRITION IN THE SAME HOST

The type of host-parasite interrelation varies widely, and many grades and types of parasitism exist. It may be expected, therefore, that the type of pathogenicity concerned will predetermine in some measure the effect of host nutrition on disease development. In order to study this matter critically, the same host (cabbage) was used with two types of parasite.

The yellows disease considered in the foregoing section belongs to the hypoplastic group of diseases. The toxic effects of undetermined materials in the invaded vessels which permeate more or less generally throughout the plant distinctly in advance of the parasite, cause chlorosis, reduced growth, wilting, and death. Clubroot of cabbage belongs to the hyperplastic group. The major

effects of the parasite on the host are essentially opposite to those of yellows. Immediately upon invasion, growth of infected tissues is stimulated rather than suppressed. Cell division proceeds more rapidly and some cells become abnormally large. Growth proceeds at the expense of tissue differentiation, and the diseased organs appear as spindle-shaped clubs or galls. Although the causal organism (*Plasmodiophora brassicae* Wor.) is an obligate parasite and can not be grown on artificial media, macerated club tissue may be used successfully as inoculum in sand-culture experiments. No inherent resistance of cabbage to clubroot similar to that in yellows is known. In view of the fact that the symptoms are primarily below the soil (or sand) line, a progressive disease development curve is not possible as in yellows. The effects must be determined at the end of a run when the plants are removed.

Pryor (12), working in this laboratory, noted a significant decrease in percentage of infected plants when the plants were deficient in potassium and an increase when they were deficient in nitrogen. At each of the four levels of nutrient concentration used in the present work, *i.e.*, $\frac{1}{10}$ basal, basal, 2 times basal, and 3 times basal, a low and a high potassium series were included. The disease index increased from $\frac{1}{10}$ basal to 2 times basal, with little difference between the latter and 3 times basal. At each nutrient concentration the index was distinctly higher at the high potassium level than at the low potassium level. When phosphorus was reduced the clubroot index decreased, whereas when nitrogen was decreased or increased the clubroot index tended to increase.

When the two diseases of cabbage, yellows and clubroot, are compared, therefore, we find that increase in salt concentration of the nutrient solution decreased the rate and degree of yellows development, on the one hand, and increased clubroot development, on the other. When the potassium-ion concentration was reduced, yellows increased and clubroot decreased in severity. When the phosphate-ion concentration was reduced, both yellows and clubroot were retarded. When the nitrate ion was reduced, yellows decreased, but clubroot increased when the nitrogen ion was increased or decreased.

SOIL REACTION

It has long been recognized that potato scab [*Actinomyces scabies* (Thax.) Güssow] is less prevalent in soils that have a reaction below pH 5.2 than in soils with a higher pH value. Keeping the reaction below pH 5.2 does not completely control but does reduce it sufficiently to be of great commercial value. In soils that are naturally highly acid, growers have learned the value of adjusting their fertilizer and lime applications so as to keep the soil reaction within the range unfavorable to scab. Application of sulfur to soils with pH above 5.2 has been used to a limited degree to reduce scab. In sandy soils, however, the benefits derived from reduced scab are often offset by reduced yield (4, 7, 10). The use of acid-forming fertilizers on soils slightly above pH 5.2 is helpful (1). In the main, the effect of high acidity has been attributed to the direct effect of the H ion upon the scab organism. The recent work of Schroeder and Albrecht (13) and of Gries *et al.* (5) has indicated that the Ca-K ratio is a factor in this

complex.   Schroeder and Albrecht (13) noted that liberal amounts of potassium as contrasted to calcium, and vice versa, resulted in increased scabbiness, although excess potassium gave more scabbiness than excess calcium.   Gries *et al.* (5) found that, both in a sandy and in a loam soil, scab increased as the Ca-K ratio was reduced by increasing the potassium and holding the calcium constant. After reaching a peak, the disease declined when the Ca-K ratio was decreased still more by decreasing calcium and holding the potassium constant.   This latter decrease occurred at a constant pH or in a range where scab might have been expected to increase.   It was suggested that one of the effects of the pH was to alter the Ca–K ratio by altering the Ca-ion concentration in the soil.

A unique use of adjustment of pH to control a disease is that arising from the work of Eddins (2) in northern Florida where the brown rot or bacterial wilt organism (*Bacterium solanacearum* EFS) builds up in the soil to a degree hazardous to potato, pepper, eggplant, and tomato.   Sulfur is added in May or June in sufficient amount to adjust the pH to 4 or below.   Cowpea or Crotalaria is grown as a summer crop, and lime is applied the following autumn in sufficient amount to readjust the pH to 5.2 for potatoes and to 5.5 to 6 for tomato, pepper, and eggplant.   In 1935, this treatment increased the yield of eggplant and tomato on severely infested lands by 10 and 15 times, respectively, when compared with untreated controls (3).

Clubroot of crucifers (*Plasmodiophora brassicae* Wor.) is the opposite of potato scab in relation to soil reaction.   In neutral or alkaline soils the disease is greatly reduced, and in some soils commercial control has been attained by application of sufficient lime to neutralize the soil solution.   The results are not always successful, however, as shown by Wellman (22) and by Larson and Walker (6). In some cases clubroot was severe even though the lime applied was sufficient to raise the pH reading to 7.0 or above.   Larson and Walker (7) found that in such a case, when the soil was removed to the greenhouse and cabbage grown in it with uniformly favorable soil moisture, disease development was prevented completely.   They suggested that the discrepancy between results in the greenhouse and in the field might be due to the fact that in limed soils under field conditions, particularly when soil moisture varied widely, the pH of the solution immediately around the roots might be lowered by the carbon dioxide given off by the roots.   This might be sufficient to permit the organism to germinate and infect the roots despite the high pH level of the solution in the soil mass.   They suggested that under greenhouse conditions with more uniform moisture the pH of the root sphere might follow more closely that of the soil solution as a whole.   Though it has not been suggested heretofore, a similar condition might prevail in potato scab, wherein the pH of the soil solution in contact with the tuber might be higher than that of the soil mass.   This might explain the occurrence of potato scab to some extent at pH levels below 5.2.   Gries *et al.* (5) have also shown that the Ca–K ratio affects clubroot.   Except at very high Ca-K levels the curve for clubroot was a mirror image of that for potato scab, a fact which suggested that the effects of calcium and potassium were inverse in the two diseases.

DISCUSSION

In a study of two distinct parasitic diseases of cabbage, quite different effects of nutrient level and nutrient balance were obtained by the sand-culture technique. In the case of the yellows disease, temperature and inherent host resistance, as well as nutrition, were shown to be interacting factors influencing the expression of disease. The importance of any one of these factors may be affected by the relative influence of the other two in a given situation. In the case of cotton wilt, it is evident that the proper balance and amount of fertilizer depress the disease, but when the soil infestation is heavy and the environment is favorable to the disease, inherent resistance in the host variety is essential for adequate control.

From the standpoint of soil management, it is best to proceed with caution in applying to the field the results obtained in greenhouse and laboratory on the effect of nutrition in relation to disease development. Even a successful field experiment on the use of fertilizer to control a given disease may yield discouraging results in a different environment, in the case of a more severe infestation by the parasite, or in the case of a host variety carrying a different degree of inherent resistance. For example, Smith and Walker (15) were able completely to control pea root rot (*Aphanomyces euteiches* Drechsler) by increasing salt concentration of a balanced nutrient in sand culture in the greenhouse. Walker and Hare (18), however, found that in heavily infested soil and under favorable environment for the disease, very heavy applications of complete fertilizer did not afford practical control. Smith (16) found that a heavy application of urea reduced wilt (*Bacterium solanacearum* EFS) of tobacco. When applied to corn as a preceding crop, this treatment offered a practical control on sandy loam soils in North Carolina. The treatment appeared to be of less value, however, on heavy soil types and on soils with a high content of organic matter. Leach and Davey (8) obtained a marked reduction in sclerotium rot [*Corticium rolfsii* (Sacc.) Curzi] of sugar beets in California by the application of nitrogenous fertilizers. The benefits derived in heavily infested fields, however, were insufficient to warrant the procedure, and as a control measure application of nitrogenous fertilizers was of value only where infestation by the fungus was light.

There is little basis to hope that, in the future, soil management and fertilization will solve any large percentage of the problems of plant disease control. There is, however, reason to believe that studies of host nutrition in relation to disease development may yield information on the basis of which modifications in soil practices may often be used to reduce the acuteness of disease losses.

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CONTROL OF PLANT DISEASES BY USE OF INORGANIC SOIL AMENDMENTS[1,2]

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An impressive list of inorganic materials has been tried at one time or other for the control of various soil-borne plant pathogens. The results of most of these trials have been negative, but a few materials have succeeded sufficiently well, at least regionally, in reducing disease incidence to have become established ingredients for use in plant disease control. A few such examples follow: The addition of sulfur to the soil provides effective control of common scab of white potatoes caused by *Actinomyces scabies* and of sweet potato pox (*Actinomyces ipomoeae*) in some locations. The use of liming materials for the control of clubroot (*Plasmodiophora brassicae*) of crucifers is a well-established practice. Compounds of mercury are often used as soil amendments for the control of such potato diseases as scab and Rhizoctonia (*Rhizoctonia solani*), or as dips or dusts for treating tubers, corms, bulbs, roots, and seeds before planting for the control of a number of diseases. Mercury also has been widely used on fine grasses for the control of several disease-producing organisms. Because of their ability to sterilize the soil immediately surrounding the seed (semesphere), copper and zinc compounds have found favor for the treatment of certain vegetable seeds, and copper has been used to some extent as a soil amendment for preventing seedling damping-off. Sodium borate has been suggested as a dipping material for use prior to the bedding of sweet potatoes where black rot (*Ceratostomella fimbriata*) is to be controlled. More recently sodium selenate used as a soil amendment has proved effective in preventing nematode infections on the foliage of chrysanthemums.

The inorganic materials most commonly used as soil amendments fall naturally into two groups. The first group, consisting of sulfur and liming materials, provide protection against certain disease-producing organisms in an indirect manner, that is, the protection afforded is derived, in part at least, through soil pH changes, rather than through the direct fungicidal activity of the amendment. The second group, comprising mercury and copper, are highly fungicidal materials, which provide protection directly by their own killing power.

Many of the inorganic soil amendments are neutralized or immobilized through chemical reaction with various soil constituents. Since these constituents fluctuate in quantity among soils, it is not surprising to find conflicting results regarding the value of a given soil amendment in different soils. The possibility

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[1] The term "amendment" is used by soil scientists for any material that is employed to correct unfavorable chemical or physical conditions in the soil. In this discussion, however, it designates also materials designed to improve biological relationships affecting the cultivated plant.

[2] Journal Series paper of the New Jersey Agricultural Experiment Station, Rutgers University, department of plant pathology.

of divergence in effectiveness is further magnified by differences in strains of the pathogene and by differences in the whole microflora, including sulfofying microorganisms, which may exist among soils. This divergence of results is well illustrated in the reports covering the use of acidifying materials and mercurials in the control of such a disease as white potato scab.

SULFUR

In a laboratory study of the *A. scabies* group, Waksman (35) found that different isolates of the pathogene varied considerably in their ability to tolerate acidity in artificial media. For example, he found that some isolates grew slowly at a pH of 4.8, whereas others made no growth below pH 5.6. The limiting pH value of the majority of strains was reported to be 5.0. Gillespie (12), as the result of a similar study, reported that growth of *A. scabies* is slower and less vigorous at pH 5.2 than at higher pH readings. In some instances, however, good growth was obtained at an initial pH of 4.8. Gillespie and Hurst (13), after examining a number of soils of different origin and type, reported that those having a hydrogen-ion concentration as low as pH 5.2 rarely produce scabby potatoes. As a result of these and many other investigations, the maintenance of a soil reaction of approximately pH 5.0, through the use of sulfur or acid-forming fertilizers, has come to be considered as a practical method of preventing excessive losses from scab along the Atlantic seaboard (4, 5, 13, 25, 26). In many other sections, however, the effectiveness of soil-acidifying materials in controlling scab is much less dependable. Aluminum sulfate was partly effective in controlling scab in western New York (34) but was of no value in Wisconsin (10), and variable results are reported by Michigan investigators (11, 37). Dippenaar (10) reported that, in Wisconsin, when H_2SO_4 was mixed with soil and used in greenhouse tests it gave good scab control, but when sulfur was used in the field at the rate of 1,200 pounds per acre it failed to control scab. Larson and others (19), who worked in this same state, reported that although sulfur treatments reduced the incidence of scab, the disease was present in appreciable amounts even after 2 years with soil pH readings below 5.0. Muncie and others (29) reported that, in Michigan, sulfur reduces scab but that the disease was present in plots showing pH readings as low as 3.5. Muncie further pointed out that the growth of *A. scabies* is only partly inhibited at low pH values "and that it gradually adapts itself to these conditions." Taubenhaus (33) reported that sulfur used at the rate of 5,000 pounds per acre on soils high in calcium gave no appreciable control of scab in Texas, and Raeder (31) reported negative results from the use of sulfur in Idaho.

From the foregoing reports, it is evident that a sulfur treatment of soil is much less satisfactory for scab control in regions where the soil is naturally near a neutral reaction than it is in the Coastal Plain soils where more acid soils prevail. Some light may have been thrown on this complex problem by Schroeder and Albrect (32), and later by Gries and associates (14), when they reported that the calcium-potassium balance in a soil is important in determining the incidence of scab. It may be, as suggested by Muncie and others (29) that strains of *A.*

scabies tolerant to low soil reactions are involved. Possibly, as indicated by the variation in the results between Dippenaar's (10) greenhouse and field experiments, the problem may involve the uniform mixing of the sulfur and the soil. Survey information gathered in New York State (1), indicates that alkaline subsoils may favor an increase in scab on potato tubers in the plowed soil. It may be that in such areas the upward movement of the soil solution during dry periods renders that portion of the soil in which the tubers develop more alkaline, temporarily at least, than soil samples taken at harvest time would indicate. It is probable that the principles involved in any or all of these suggestions and perhaps additional ones are concerned.

LIMING MATERIALS

For many years liming materials have been known to exert a suppressive influence on the occurrence and severity of clubroot, a disease that affects the roots of nearly all members of the cruciferous family. Wellman (36) has presented an excellent review of the literature on this subject up to 1930. In this same publication he presented the results of his own informative experiments. As a result of a survey made in Wisconsin, Illinois, and Indiana and experiments conducted in the greenhouse and in the field, he concluded that hydrated lime [$Ca(OH)_2$], when mixed in the soil in adequate quantities, will give excellent control of this disease. He also reported that calcium carbonate was less effective than the hydroxide in preventing the occurrence of clubroot, whereas potassium carbonate used in quantities sufficient to give a pH value of 8.1 failed to inhibit the disease. In one instance, soil at a pH of 7.2 that was treated with $Ca(OH)_2$ prevented the development of the disease when a pH change of only 0.1 was made, whereas $CaCO_3$ did not inhibit clubroot until a pH value of 7.9 was reached. From these and other considerations Wellman concluded that the H-ion concentration was not the limiting factor for the disease, but that "The toxicity of calcium hydroxide to the parasite seems to be due to a definite poisoning action on the organism by this chemical compound. The inhibiting effect produced on this disease by limes is apparently not correlated with the amount of Ca ions applied or the number of active OH ions observed through pH-determination studies of the soil."

On the basis of a carefully controlled experiment, Chupp (3) reported that where $Ca(OH)_2$ was used in either sandy clay soil from New Jersey or dark loam from New York, complete control of this disease occurred at 7.4, whereas clubroot became increasingly severe below this pH reading. In 1939 Haenseler (16) reported that when Ca, Mg, K, or Na oxides, hydroxides, or carbonates were used in quantities equivalent to 1,000 and 2,000 pounds of CaO per acre, marked decreases in injury from the disease were obtained in all plots where the soil pH value was maintained at 7.0 or above, regardless of the cation used. In general, the carbonates gave more satisfactory results than the oxides or the hydroxides. Gries and associates (14) concluded from an investigation of the effect of Ca-K ratios on the development of clubroot that the disease decreases as the pH value is increased and that at any pH level as the concentration of the calcium ion increases the severity of the disease decreases.

From the foregoing investigations it seems evident that liming materials have a suppressive effect on *Plasmodiophora brassicae* and that under some conditions $Ca(OH)_2$ is more effective than the carbonate, whereas under other conditions these two materials may be used with about equal effectiveness. It also seems likely that both the hydroxyl and the calcium ions play a part in this suppression. The effect of the hydroxyl ions seems to predominate under the conditions existing in some soils, whereas under other conditions the calcium ion or the Ca and the OH ions jointly seem to exert the suppressive influence.

Although the above experimental data seem to be somewhat contradictory, it is probable that the explanation for these apparent contradictions lies in our own inability to understand all factors operative in complex soil environments in which the work is conducted. The variation or lack of variation in the relative effectiveness of $Ca(OH)_2$ and $CaCO_3$ among soils is probably not surprising when we consider the fact that in soils having a high CO_2 pressure the $Ca(OH)_2$ might in a very short time be almost wholly converted to $CaCO_3$ or $CaHCO_3$, whereas in other soils low in moisture or CO_2 this conversion to the carbonate or bicarbonate may require considerable time. Under the latter conditions the extreme pH changes induced by hydrated lime would be expected to exert a maximum influence, since the high pH levels would be maintained for a maximum length of time.

Calcium cyanamide (a commercial product, which is a mixture consisting mainly of calcium cyanamide, carbon, and calcium oxide) has been shown by several investigators to have a marked influence on the microflora and microfauna of the soil. As stated by Haenseler and Moyer (15), "The effects on the organisms may be either stimulative or depressive in nature and seem to be determined to a considerable extent by the soil reaction, the soil type, the quantity of calcium cyanamide applied, and the specific organism involved."

The fact that the effect of calcium cyanamide is influenced by the hydrogen-ion concentration of the soil is well explained by Crowther and Richardson (6) in their discussion dealing with the decomposition of calcium cyanamide in the soil. In this discussion it is pointed out that calcium cyanamide in a water solution forms, among other things, free cyanamide:

$$CaCN_2 + H_2O \rightarrow H_2CN_2 + CaO$$

In an alkaline solution, free cyanamide polymerizes almost quantitatively to

$$NH_2$$
$$|$$

dicyanodiamide, $C==NH$, whereas in an acid solution free cyanamide is hydro-

$$|$$
$$CH \cdot CN$$

$$NH_2$$
$$/$$

lized to urea, $O==C$. With this variation in decomposition products it is

$$\backslash$$
$$NH_2$$

not surprising to find the following statements (15) in the literature dealing with calcium cyanamide: "A greater decrease in the number of fungi resulted in soils

which were near the neutral point in soil reaction than in soils which were more acid"; and, again, "The effect of calcium cyanamide on the soil microflora seemed to be more closely correlated with the soil reaction than with the quantity of the material used."

As the result of these investigations Haenseler and Moyer (15) made the following statement: "In greenhouse tests, calcium cyanamide was about two and one-half times as effective as an equal quantity of hydrated lime in controlling clubroot infection shortly after application." In addition to the possible value of calcium cyanamide in clubroot control, these investigators found it to be of value in reducing seed decay and seedling damping-off when incorporated in the soil or used as a side-dressing. The margin of safety between control and seed injury, however, was found to be small.

COPPER

It is not surprising to find evidence that when copper compounds are used in the soil for protection against plant parasites, their value as fungicides varies considerably. Not only does their protective value vary among soils, but the occurrence and severity of plant injury likewise vary. As early as 1898 Halsted (17) reported that copper compounds, when mixed in the soil, gave variable results in the control of potato scab, and Lutman and Cunningham (21) reported no control from the use of such compounds in experiments conducted in Vermont. That the soil and compounds within the soil markedly affect the degree of injury from the use of copper is illustrated by the well-known fact that less red copper oxide should be dusted on seeds that are to be planted in light soil than on those to be planted in soils containing a considerable quantity of clay or organic matter. Poole (30) reported that when sweet potato sprouts were dipped in a 20-20-50 bordeaux mixture just before being set in the field, good control of stem rot (*Fusarium hyperoxysporum*) was obtained. In New Jersey it has been found that the value of the treatment may be modified by soil factors which influence copper solubility, such as hydrogen-ion concentration or adsorptive capacity.

In an experiment conducted in New Jersey, sweet potato sprouts treated with a 20-20-50 bordeaux mixture and untreated check plants were set in a light sandy loam soil having a pH value of 4.8 and in Sassafras loam having a pH of 7.0. All plants used in this experiment, with the exception of the treated sprouts set in the sandy loam soil, started well. The plants in this treatment started with considerable difficulty, and 5 per cent of them died as a result of injury. After these plants became established, however, they also made good growth.

When the plants were harvested, an examination revealed 53 per cent scurf-infected potatoes on the untreated plants grown in the sandy loam soil and only 7 per cent infected potatoes on the treated plants on the same soil. In Sassafras loam the counts made on the fleshy roots taken from the untreated plants revealed 77 per cent scurf, whereas the treated plants produced a crop of which 46 per cent showed scurf.

Although the soil factors responsible for the differences in plant toxicity and disease control were not determined in this experiment, it would appear that the

acid soil reaction in the sandy loam is sufficient to increase significantly the solubility of the copper, as compared with the neutral soil. The differences in copper solubility between the two soils might be further enhanced by the fact that the heavier Sassafras loam possessed considerably higher copper-adsorptive powers than did the sandy loam.

The effects of such factors as soil pH and organic matter content on the activity of copper were further illustrated in an experiment conducted by Haenseler and Hammer, the results of which have not heretofore been published. In this experiment Sassafras loam having a pH value of 5.4 was mixed with various amounts of $CuSO_4$ and placed in pots. Another quantity of this soil was made neutral in reaction, with lime, after which it was mixed with various quantities of $CuSO_4$ and placed in earthenware crocks. A third series was similarly prepared from a soil high in organic matter (peat) having a pH of about 6.0. Cowpeas were then planted in all pots. Germination was retarded greatly in the acid soil when more than 400 pounds of $CuSO_4$ per acre was used. In the neutral soil, retardation of germination resulted when more than 800 pounds of $CuSO_4$ per acre was used. Retardation in germination was less evident in the soil high in organic matter than in either of the more highly mineral soils. Growth of the cowpeas was retarded in the acid Sassafras loam when 200 pounds or more of $CuSO_4$ per acre was used, whereas in the neutral soils equal retardation did not occur until 1,600 pounds of $CuSO_4$ was used. In the peat soil, $CuSO_4$ at the rate of 6,400 pounds per acre did not retard growth.

A recent investigation by Martin and Leach (24) on the influence of certain proteins and protein decomposition products on the solubility of cuprous oxide in relation to its toxicity as a fungicide revealed that products of protein decomposition may markedly increase the solubility of this copper compound. For example, doubly distilled water dissolved from 0.6 to 0.8 p.p.m. of copper from yellow cuprous oxide during a 7-day period. When glycine was added to the distilled water at the rate of 1 gm. in 100 cc., enough of the cuprous oxide was dissolved to bring the copper content of the solution to 2,200 p.p.m. It was also discovered that "The copper liberated by these nitrogenous compounds is equally as toxic as the copper dissolved in distilled water provided no excess of nitrogenous compounds is present. However, the threshold of toxicity in p.p.m. is greatly increased when an excess of these compounds is present, 1 per cent glycine raising the toxicity threshold from 0.3 p.p.m. to 225 p.p.m."

As a result of recent studies, Linn (20) and Marsh (23) report that when calcium chloride, magnesium chloride, or potassium chloride is present in the media with copper in excessive amounts it, like the protein decomposition products, exerts a depressing effect upon the toxicity of copper to certain fungi. Though their investigations cover concentrations much lower than those which exist in soils, this antidotal action may be of importance in determining the efficiency of such fungicides as copper or mercury in a soil.

Since inorganic salts and products of protein decomposition are common constituents of soils, it seems reasonable to expect that such products, together with the composition and the pH value of the soil, would influence the solubility

and toxicity of copper compounds used as soil amendments or as seed or sprout treatments in the soil. The interactions of these several variables may account for some of the variability in protection and injury experienced with copper compounds in soils.

<div align="center">MERCURY</div>

Experiments with mercury for the control of such diseases as scab and Rhizoctonia of white potatoes and scab of gladiolus (*Phytomonas marginata*) have given erratic results. Two experiments conducted in New Jersey will amply illustrate this fact.

In one field, calomel at the rate of 6 pounds per acre was applied with the fertilizer. At harvest time 89.3 per cent of the potatoes from the calomel-treated rows were free from scab, and only 2.2 per cent were unsalable, whereas untreated rows produced potatoes of which only 32.8 per cent were free of scab and 37.4 per cent unsalable. In another field, the potatoes harvested from rows treated with calomel at the rate of 5 pounds per acre, applied in the fertilizer, produced potatoes that were 97.4 per cent scabby, of which 82 per cent were unsalable. In this field the rows that were not treated with calomel produced potatoes that were 59.2 per cent scabby, of which 11.5 per cent were unsalable. The results of these two experiments are characteristic of those from other sections. Investigations in New Jersey (27), Long Island (7), and Canada (22) report excellent results in the control of potato scab from the use of mercurials, whereas upstate New York (34), Michigan (18), and parts of New Jersey (28) report no control following their use. In fact, as illustrated in the New Jersey data presented above, in many of these sections not only do the mercurials fail to control scab, but an actual increase in scab may follow their use.

In an investigation of the effects of calomel on potato scab as influenced by sources of soil and of *A. scabies* inoculum, KenKnight (18) found that calomel had a controlling effect on scab when potatoes were grown in pots of Long Island soils that had not been artificially inoculated. Calomel-treated soil from the same locality produced significantly more scab, however, than did untreated soil when Michigan strains of *A. scabies* were used. This variation between areas, in respect to scab control, may be markedly influenced by the strains of the pathogen concerned, as illustrated by the following significant statements by KenKnight:

In local [Michigan] soil that had been fumigated with carbon disulphide and desiccated, calomel caused increases in scabbing, giving significant differences at 50 and 350 p.p.m.

In Long Island soil that had been steamed and infested with Michigan strains of *Actinomyces*, calomel at 50 and 350 p.p.m. had no appreciable effect on scabbing while 1,000 p.p.m. gave a highly significant increase.

In Long Island soil that had been steamed to remove contamination and reinfested with strains of *Actinomyces* from Long Island, calomel at 1,000 p.p.m. gave complete control of scab.

In local [Michigan] soil that had been sterilized and infested with Long Island strains of *Actinomyces* calomel caused a significant reduction in scabbing at all rates of treatment, virtually eliminating scab at 1,000 p.p.m.

That these variations in the effectiveness of mercurials in the control of scab are due largely to a variation in tolerance to mercury by strains of parasitic *Actinomyces* is further shown (18) by the fact that some of the isolates from Michigan tolerated a concentration of mercuric chloride more than 100 times that of certain isolates from regions where mercurials are effective. KenKnight further reported that the population of *Actinomyces* in Michigan soil infested with local strains gave an initial reduction in numbers "but that those that could tolerate the mercurials multiplied apparently as a result of reduction in competition from other organisms." This last statement may explain why mercurials actually increase the incidence and severity of scab in some soils. It seems likely that this treatment, by reducing competition, allows for an actual increase in the numbers of parasitic *Actinomyces*.

TABLE 1

Effect of soils and the placement of mercurials in controlling rhizoctonia stem lesions on potatoes

TREATMENT NUMBER	SOIL*	LOCATION OF HgO	CONDITION OF POTATO STEMS		
			Healthy	Slight to medium cankers	Severely cankered or cut off
			per cent	per cent	per cent
1	A	1 inch below and 1 inch to side of seed piece	66.7	23.8	9.5
2	A	As in treatment 1, but mercurial separated from seed by 1 inch air space	50.1	32.6	17.3
3	A	Mixed through soil	90.0	10.0	0.0
4	A	Check, no Hg	20.0	28.0	52.0
5	B	As in treatment 1	6.7	13.3	80.0
6	B	As in treatment 2	5.1	11.6	83.3
7	B	As in treatment 3	68.8	25.0	6.2
8	B	Check, no Hg	0.0	18.2	81.8

* Soil A, Sassafras loam; soil B, a dark sandy loam containing greensand marl.

Although a variation in the strains of the pathogene present in a soil is undoubtedly of importance when dealing with the effectiveness of a soil amendment, so too are those soil factors that influence the availability, mobility, and chemical state of the disinfesting agent used. Soils containing ingredients capable of precipitating or binding the quantity of mercury used, leaving only slightly available compounds or complex formations, would undoubtedly adversely affect the disinfecting value of a mercurial. The failure of mercurials to offer protection may be pronounced when they are placed some distance from the zone where protection is needed, as is the case where mercury is applied in the fertilizer band 2 to 3 inches away from the potato seed piece.

The effect on disease control of immobilizing the mercury is illustrated in table 1. In this experiment Sassafras loam, in which mercury is effective as a fungicide, was placed in 2-gallon pots and planted, at a depth of 4 inches, with

potato seed pieces severely spotted with Rhizoctonia sclerotia. In treatment 1, calomel at the rate of 25 p.p.m. (based on total soil in pot) was placed in a band 1 inch below and 1 inch to the side of the seed pieces. In treatment 2, the mercury was also placed below and to the side of the seed pieces; however, in this case the soil in which the mercury was placed was separated by a 1-inch dead air space, by means of a screen, from the soil in which the potato sets were planted. In treatment 3, the mercurial was mixed throughout the body of the soil. In treatment 4, no mercurial was used. Treatments 5, 6, 7, and 8 are replications of treatments 1, 2, 3, and 4 with the exception that in these instances a dark sandy loam (soil B) containing large quantities of greensand marl was used. In this soil, a mercury treatment, as used in the field, has never been of much value. In this experiment, mercurials were uniformly effective in soil A, regardless of placement. The fact that a separation by a dead air space from the soil in which the seed piece was growing (treatment 2) failed to impair to a serious degree the efficiency of the mercurial, demonstrates the significance of vapors as a mobile form of mercury in the soil. Undoubtedly mercury in solution also is an important migrating form in some soils. In soil B, the failure to provide protection when the mercury was placed a short distance from the seed piece (treatments 5 and 6), while providing protection when it was mixed in the soil around the seed piece (treatment 7), demonstrates the power of some soils to prevent effective migration of mercury.

In an experiment conducted by R. P. White and the author, gladiolus corms severely infested with scab, a bacterial disease, were dipped in a suspension of calomel used at the strength of 1 pound in $2\frac{1}{2}$ gallons of water, than planted in soil A (Sassafras loam) from New Jersey and soil C (Volusia) from New York. Untreated corms were also planted in pots containing these same soils. In this experiment the mercury-dip treatment provided excellent protection in soil A but failed to control the disease in soil C, despite the fact that the mercury was deposited on the surface of the corms. Where these same two soils were used in a Rhizoctonia stem lesion control experiment, the results were similar to those reported for gladiolus scab. Calomel (25 p.p.m.) mixed through the soil gave good control in soil A and only poor to mild protection in soil C.

In these experiments we have seen that there are soils (A) in which mercurials are effective, whether they are separated from the potato seed piece by a short distance or placed in the exact location where fungicidal protection is needed. There are other soils (B) in which mercurials are incapable of migrating 2 to 3 inches in quantities sufficient to be effective, but will provide protection against stem cankers when the fungicide is placed in the immediate location where fungicidal protection is to be offered. There are also soils (C) in which the effectiveness of the mercurial is largely destroyed even when placed in the location where protection is to be offered. In this connection the mercury-binding power of these soils against water leaching seems to be significant. Twenty-five grams of air-dried soil C will bind 0.2070 gm. of mercury as $HgNO_3$, whereas soil B holds 0.1380 gm. and soil A immobilizes 0.0460 gm. before allowing mercury to be washed from the soil in the water leachate.

An example of what appears to be the reduction of mercurial efficaciousness

by straight precipitation was encountered in a part of a field in which sulfur had been recently mixed through the soil to a depth of 3 to 4 inches. In this part of the field a mercurial was less effective than where sulfur had not been applied. Perhaps some of the effectiveness of the mercurial was destroyed by the production of a most stable form of mercury, the sulfide.

Another factor in addition to mercury-binding or precipitation by the soil seems to influence the effectiveness of a mercurial under some conditions. For example, if an oxidizing material such as potassium permanganate is mixed with the soil in which the calomel is placed in treatments 1 or 2 (table 1), the effectiveness of the mercurial is largely destroyed. The same is true if the potassium permanganate is mixed in soil located in a layer between the mercurial and the seed piece. On the other hand, when metallic zinc is mixed with the calomel in treatments 1 and 2, the effectiveness of the treatment is increased. Perhaps the action of the zinc is to convert calomel into metallic mercury, which would have the effect of increasing the volume of mercury vapor (8).[3] These views in general have been substantiated by Booer (2).

NEW DEVELOPMENTS

Dimock (9) recently reported that sodium selenate used as a soil treatment gave excellent control of foliar nematodes of chrysanthemums. Though selenates are extremely toxic to animals, they may be useful for protection of ornamental plants.

In preliminary experiments evidence has been obtained which indicates that when disodium ethylene bisdithicarbamate is mixed in the soil in which certain plants are growing, not only are diseases affecting the roots controlled, but sufficient amendment is translocated to the foliage to offer some protection against certain foliage diseases and insect pests. If, as this suggests, foliage diseases can be controlled by the use of soil amendments that are nontoxic to humans, then a new approach to plant protection becomes available to us.

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VOLATILE SOIL FUMIGANTS FOR PLANT DISEASE CONTROL

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There are a number of important pathogens that can attack a variety of host plants, that persist in the soil for many years, and that cannot always be controlled economically by rotations, by a change in growing methods, or by the use of resistant varieties. Moreover, not infrequently a new or hitherto unreported soil-borne disease breaks out in a new area and threatens a widely grown crop, like the bulb nematode, *Ditylenchus dipsaci*, in certain onion regions of New York; the southern Sclerotium rot of sugar beet, *S. rolfsii*, in California; the golden nematode, *Heterodera rostochiensis*, in potato fields of Long Island; the Phymoto-tricum root rot in sections of the South; and the root-knot nematode, *Heterodera marioni*, and the sugar-beet nematode, *H. schactii*, in various parts of the world.

An efficient, cheap soil treatment to eradicate new or local outbreaks before they become widespread and to aid in the control of old established ones would be most welcome. Though the greatest need is for a cheap nemacide, the treatment would be more useful if it could also be employed against fungi in the genera Armellaria, Botrytis, Fusarium, Omphalia, Plasmodiophora, Thielavia, Verticillium, Pythium, Rhizoctonia, Phytophthora, and Sclerotinia.

Certain soil disinfestants[1] such as formaldehyde, carbon disulfide, and hydrogen cyanide have been employed on a small scale for years in the form of aqueous drenches, emulsions, or solutions. It has been assumed that the water was necessary to bring about penetration and contact with all parts of the soil. The large quantities of water required, 20,000 to 40,000 gallons per acre, the labor of applying drenches, and the expense of $300 to $600 an acre, all limit the drench method to land growing crops of high value.

The application of undiluted, volatile fumigants by regularly spaced injections or by subsurface parallel streams offers an easier, less expensive, more rapid way of treating large areas of soil which have been uneconomical to treat hitherto. Extension of the method will depend on finding cheaper fumigants and on further studies of the factors governing their successful employment.

THE IDEAL SOIL FUMIGANT

Like steam, the perfect soil fumigant should be able to kill a variety of microorganisms, insects, and weed seeds. It should be inexpensive, noninflammable, easy to handle, and harmless to the operator and the equipment employed. It should be quick to penetrate and do its work, both deeply and on the surface layers, yet quick to leave the soil or else be harmless to subsequent plant growth. It should not be so phytocidal that its fumes are harmful to living plants near by, nor so unstable that it can not be stored easily and safely. No substance yet

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[1] Since soil does not become infected with nematodes or fungi any more than a lake becomes infected with fish or weeds, but merely infested, soil fumigants are therefore not used as disinfectants, but as disinfestants.

meets all of these requirements, but several have been or are being developed which are suitable for specific pests and cheap enough to meet some of today's needs.

METHODS OF TESTING VOLATILE SOIL FUMIGANTS

O'Kane (9) seems to have been one of the first to study the diffusion pattern of a fumigant injected into soil. He found that a 3-dram dose of carbon disulfide was lethal to ants buried a maximum lateral distance of 4 or 5 inches from the point of injection. Several workers have employed similar techniques with different fungi, in culture and as sclerotia, with infected roots, bulbs, and seeds, and with nematodes for test organisms. Chitwood (4) thus found the maximum

TABLE 1

Comparison of several soil fumigants in the control of the root-knot nematode

TREATMENTS	DOSAGE*	MEAN NUMBER ROOT GALLS ON TEST PLANTS IN 6 WEEKS
	ml.	
Checks....................................	....	440.0
	18.50	599.0
Propylene dichloride......................	8.25	336.0
	12.50	176.0
	1.25	97.0
Dichlorisopropyl ether....................	2.50	65.0
	5.00	0.6
	3.00	37.0
Dowfume G.†.............................	4.00	16.0
	5.00	2.6
	1.25	27.0
Dichlorethyl ether.......................	2.50	3.4
	5.00	....‡

* Amount on 10-inch centers.

† A 3 to 1 mixture of ethylene dichloride and carbon tetrachloride containing 10 per cent methyl bromide.

‡ Too toxic for any plant growth for months.

killing range, or k value, for a 2-ml. dose of chloropicrin against the bulb nematode *Ditylenchus dipsaci* in a sandy soil, under certain moisture and temperature conditions, to be about 6 inches. He showed that the upper 8 inches of soil can be fumigated with a minimum of overlapping if the injections are made at the corners of contiguous equilateral triangles of such size that their centers are at a distance from each corner equal to the maximum effective killing range for the chemical and dosage employed. Thus the most efficient ultilization of any chemical, in terms of horizontal spacing, is obtained when application points are located in straight parallel rows 1.5 k apart, and when injection points in each row are 1.732 k apart. Each injection will then fumigate an area 2.598 k^2. If k is expressed in inches, then the number of applications per acre will be 2,414,411 ÷ k^2, and similarly the number per square yard will be 498.8 ÷ k^2.

A value for k of 6 inches dictates the spacing of application points 10.4 inches apart in rows 9 inches apart for complete coverage with least overlapping. This spacing of the injections for chloropicrin has become standard practice in the Northeast. In the drier, warmer sections of the South and West a 12-inch spacing is generally considered adequate.

Like O'Kane, Chitwood found that horizontal and vertical k values were not identical. The lethal pattern about an injection point becomes somewhat pear-shaped, which perhaps is to be expected of a gas heavier than air, and may account for occasional failure to kill all nemas in the first inch or two of soil.

The writer's students, Stark and Lear, have done pilot testing of several chemicals in a variety of soils and under various temperature and moisture conditions in 1-gallon glazed crocks. The results of two of these tests are given in tables 1

TABLE 2

Nemacidal action and toxicity of some potential soil fumigants

TREATMENT	DOSAGE	MEAN NUMBER OF WEEDS	MEAN HEIGHT OF TOMATOES	MEAN NUMBER OF NEMATODE GALLS IN 6 WEEKS
	ml.		*inches*	
Check............................	0	17	12	177.25
1,1-Dichloroethane................	7.5	17	9	88.25
	12.0	18	12	1.25
Dowfume G........................	7.5	8	12	0.25
Ethylene dichloride...............	12.0	13	10	0.25
Xylene...........................	8.5	10	11	0
	17.0	8	14	0
	1.25	24	10	0.50
	2.50	9	9	0
Ethylene dibromide...............	3.75	6	8	0
	5.00	7	9	0

and 2. Following these crock tests it has been found advisable to make tests of the phytocidal properties and persistence of the better fumigants in the soil before taking them to a commercial greenhouse for small plot testing under the conditions a grower must cope with. These semifinal tests are more valuable if they can be made both summer and winter.

FACTORS AFFECTING EFFICIENCY OF A SOIL FUMIGANT

The role played by adsorption and by some other factors has recently been studied by Stark[2] in connection with chloropicrin and other fumigants. For this he used a gas-tight chamber in which was placed a weighed quantity of soil on a molybdenum pan suspended by a very sensitive molybdenum wire spring. A measured quantity of the fumigant was introduced into a wick suspended in the chamber. Subsequent stretching of the spring, previously calibrated with

[2] Stark, F. L., Jr. Investigations relevant to the use of chloropicrin for soil fumigation. Thesis, Cornell University, 1945.

known weights, furnished a direct measure of the amount of gas adsorbed by the soil. This elongation was observed and measured by means of a cathetometer.

Stark found that the ratios adsorbed by particles of soil of different sizes were as follows, when that adsorbed by very find sand (particle size 20 to 246μ) was taken as unity: silt (particle size 2 to 20μ) 4, clay (size 1 to 2μ) 12, and colloidal clay (size $< 0.5\mu$) 36. Stated differently, the dry sand fraction of a mineral soil could adsorb from a given initial concentration of chloropicrin up to 0.18 per cent of its weight at $30°$ C., whereas the silt fraction could adsorb 0.8 per cent, the clay 3.2 per cent, and the colloidal clay fraction nearly 10 per cent of its dry weight. This means that the amount of gas adsorbed by any soil is largely dependent upon the size of the clay fraction. The process is exothermic, reversible, unimolecular, and with the clay fraction almost linear in relation to temperature, though at low temperatures some capillary condensation may occur to increase the amount adsorbed. Stark found that the process was less pronounced at higher humidities but was not affected by aggregation of the soil particles, by changes in pH, or by the presence of organic matter in the form of dry muck, peat, or horse manure.

In comparing the lethal action of chloropicrin in soils of three textures, each at three different temperatures and three moisture levels, Stark found that the higher the clay fraction, the better was the survival of the test organism (wheat) and hence the less toxic was the chloropicrin at a given dosage rate. Furthermore, additions of ground charcoal to a soil completely inhibited the toxic action of a certain dosage of the gas. The three factors governing adsorption were found, therefore, to be the size of the soil particles, the soil temperature, and the concentration of the gas. The amount of adsorption of different fumigants seemed to be related to their boiling points. Thus chloropicrin (boiling point $113°$ C.) was more highly adsorbed than ethylene dichloride (boiling point $83°$), and carbon disulfide (boiling point $46°$) was adsorbed least of all three.

Stark found a significant reduction in efficacy when the soil temperature at the time of treatment was reduced from $85°$ F. to $73°$ F. High soil moisture content reduced effectiveness markedly. A moisture content amounting to 10 or 15 per cent of the soil capacity, he believed to be optimum for maximum lethal effect.

Withholding the water seal for as much as 2 hours after the chloropicrin was injected resulted in as poor control as though no seal was applied. A water seal was found to be more important on light sandy soil than on heavy. A seal made by 12 gallons to 100 square feet (roughly 1 pint per square foot) was as good as one in which twice this amount of water was employed. Some of these findings of Stark are already known to hold for certain other soil fumigants.

CHLOROPICRIN

Ever since the work of Johnson (6), chloropicrin has become, for lack of a better one, a yardstick by which other fumigants are measured. It exhibits fungicidal and herbacidal properties to a considerable degree at the lethal dosage rates employed for the control of nematodes. It lacks the fire hazard of carbon disulfide but is corrosive to metals, can cause skin burns, and is extremely phytocidal.

Its lacrimating and vomiting features are variously heralded as an unmitigated evil and a good safety feature. But all agree expense prevents its greater use on land devoted to low-value crops, as does also the necessity of providing a water or other type seal for a day or two after treatment.

As commonly employed in greenhouses, for potting soil, composts, coldframes, and occasionally field soils, it is injected 3 to 6 inches deep in holes 9 to 12 inches apart, or in continuous flow beneath the soil in rows 10 inches apart at the rate of 200 to 600 pounds per acre. A standard dose is from 2 to 4 ml. per injection on 10- to 12-inch centers. Impervious covers for treated soil, such as a gasproof cloth for compost piles, glue-coated paper for seedbeds, and closed containers for potting and mushroom casing soils, are recommended. Where these are unobtainable, a water seal, obtained by sprinkling the surface, has given about 85 per cent as good results according to Godfrey and Young (5). The majority of commercial jobs of soil fumigation are sealed this way now.

A 48-hour period of confinement is long enough for maximum results with chloropicrin. It may be safe to plant treated soil with some seeds in a week, but seedlings cannot be transplanted into treated soil until all odor of the gas has disappeared. Hot, dry conditions and stirring hasten its escape. The sclerotia-forming fungi are somewhat difficult to kill, particularly if their sclerotia are in a dry condition at the time of treatment. The work of Stark and others indicates that whenever the soil is below 65° F., or is too wet, or contains considerable clay or when adequate facilities for prompt covering are not available it is well to increase the dosage rate by 50 to 150 per cent.

CARBON DISULFIDE

Were it not for its inflammable and somewhat disagreeable nature, carbon disulfide might find more favor, for it is a moderately good nemacide and not very expensive. Bliss (1) in California, and Godfrey and Young (5), in Texas, have rated it as a fairly good fungicide, and tree roots are more tolerant to it than to some other fumigants. Some workers have reported good control of root-knot nematode from applications as low as 500 pounds per acre in seedbeds, although 1,000 pounds is a more commonly mentioned figure where deeper control is needed. This is 8.25 ml. per injection per square foot and would cost approximately $90 an acre. It is said to take a ton to the acre to kill dry sclerotia of *Sclerotium rolfsii*.

For best results with lowest dosage rates the ground should be covered with gasproof paper or a water seal. However, in California where carbon disulfide is used as a weed killer it is sometimes applied by means of a mechanical subsoil injector followed by a rut filler and a heavy roller which seems to reduce the need for special cover.

DD MIXTURE

The announcement of Carter (2), that DD mixture was doing the work of controlling root knot on pineapples in Hawaii at much less expense than chloropicrin, aroused widespread interest in this petroleum industry by-product in the

manufacture of allyl alcohol. In the crude form, composition of which may be varied somewhat, the mixture is said to contain approximately 33 per cent 1,2-dichloropropane and 63 per cent 1,3-dichloropropylene with about 5 per cent of higher-boiling trichlorides of propane. It has a boiling range of 95° to 150° F., which means it is less volatile than several other fumigants.

In our tests and from correspondence with others who have used it we have concluded that DD mixture is an excellent nemacide when used in sufficient quantity, 500–700 pounds per acre ($75–$105),[3] but that it has rather limited fungicidal and herbacidal properties. It may remain in the soil for rather long periods of time, often to the detriment of subsequent crop growth.

TABLE 3

Yield of fall tomatoes and control of root-knot nematode obtained with several soil fumigants in a commercial greenhouse

FUMIGANT	DOSAGE* PER INJECTION ON 10-INCH CENTERS	FRUIT OBTAINED PER PLANT	MEAN AMOUNT OF GALL FORMATION ON ROOTS†
	ml.	*lbs.*	
Check...................................	....	4.54	2.80
DD mixture..............................	4.18	5.45	1.25
Chloropicrin.............................	1.61	5.50	0.95
	2.58	5.67	0.98
Chloropicrin + ethylene dichloride (1–9)....	7.35	5.35	0.99
Chloropicrin + methyl bromide (3–1).......	1.80	5.80	0.96
	4.19	5.65	0.70
Dowfume G (10 per cent CH₃Br)..........	6.16	5.38	0.67
	8.64	5.47	0.76
Least difference required for odds 19:1....................		0.66	0.72
99:1..................		0.89	0.97

* For an indication of equivalent rates in pounds per acre and for costs of materials see table 5.

† Roots in the five replicated plots were scored by a system in which 0 means no infection and 4.00 means maximum possible. Anything below 1 represents satisfactory control.

In a recent experiment performed by Lear and Stark in which DD was compared with chloropicrin and Dowfume G (containing 10 per cent methyl bromide) for depth of penetration in barrels of soil infested with root knot, DD mixture killed nearly all nemas to a depth of 27 inches, or the bottom of the barrel, whereas standard dosages of the other two were lethal to depths of only 10 or 12 inches. This faculty could be of great value in the treatment of old greenhouse soil heavily infested with nemas to a depth of several feet. It might also be very useful in the control of the sugar-beet nematode, where Thorne (14) has shown that one of the biggest obstacles to successful chemical control has been the inability of chemicals, calcium cyanide in particular, to penetrate and kill the 13 per cent of the nematode population which he found resided below the first foot.

[3] Price of 15 cents a pound is an estimate based on conversations with company officials.

Another of the hopeful features about DD mixture is that its higher boiling range or lower volatility make it unnecessary to cover treated soil with even a water seal, which, if true under all circumstances, is a matter of considerable importance. The results of a greenhouse test of four fumigants including DD mixture are summarized in table 3. Tests made with propylene dichloride have shown this constituent of DD mixture not to be nemacidal (see table 1), from which it may be concluded that this property is derived from the 1,3-dichloro-propylene.

G. K. Parris[4] has made over a dozen tests with DD as a fungicide and nemacide at Norfolk, Virginia. He obtained excellent control of root knot nematodes by applications as low as 200 to 400 pounds per acre with holes spaced 12 inches apart and found control to last for more than 9 months. Even 500 pounds per acre, however, failed to control weeds, and 1,000 pounds failed to control damping-off due to Rhizoctonia, Fusarium, or Pythium. Unless soil was warm, phytocidal effects of treatment lasted for several weeks.

Other high-boiling-point materials that seem, from preliminary tests, to have similar abilities to control nematodes include pentachlorethane, tetrachlorethane, dichlorisopropyl ether, and ethylene dibromide. Some of them are powerful nemacides but are also very phytocidal, necessitating long intervals between the time of treatment and replanting, a disadvantage which denies them a place in greenhouse work but may not unfit them for use out of doors in warm climates.

ETHYLENE DICHLORIDE

Ethylene dichloride is a cheap solvent for oils, waxes, and certain alkaloids and is widely used as a constituent of some insecticidal fumigants. Although the effective dosage rate against nematodes is five to seven times as large as that of chloropicrin (10 to 15 ml. per square foot), nevertheless the cost per unit area of soil is less than half as high, according to Chitwood (3). It has other advantages, since it is not disagreeable to handle, not corrosive to metals or skin, and not very phytocidal. Its main drawbacks are that it is not a good fungicide, that it does not kill weed seeds very well, and that it requires nearly a ton to the acre to kill nematodes.

Mixtures of ethylene dichloride and chloropicrin have given good nematode control at intermediate costs, according to Newhall and Stark (8). The proportion used has usually been a 9-to-1 mixture, which still possesses all the bad features of straight chloropicrin and fails to reduce the cost of treatment enough to make it very worthwhile.

In two field tests against the onion-bulb nematode, *Ditylenchus dipsaci*, made on muck land, the writer obtained very good control with applications as low as 6 ml. on 10-inch centers, or an expenditure of approximately $90 an acre. It is unfortunate, since it is abundant and cheap, that the related compound, propylene dichloride, shows no nemacidal properties (table 1).

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[4] Summarized here from unpublished data with his kind permission. Since this article was prepared, the following paper has been published: PARRIS, G. K. 1945 The nematocidal and fungicidal value of D-D mixture and other soil fumigants. *Phytopath.* 35: 771–780.

METHYL BROMIDE

The noninflammable, noncorrosive fumigant methyl bromide has been rapidly exploited since its first use in France 12 years ago. Its low boiling point, 4.6° C., and high volatility, 1,824 mm. vapor pressure at 25° C., enable it to penetrate rapidly and adapt it to fumigation work at lower temperatures than some other fumigants. Many plants can stand concentrations of more than a pound to 1,000 cubic feet, and it has some herbacidal and fungicidal properties in addition to its high toxicity to nematodes and insects.

Since Taylor and McBeth (12) first showed that, if this fumigant was confined under a gasproof (glue-coated paper) cover, the root knot nematode could be destroyed in an outdoor seedbed by the introduction of 80 ml. per cubic meter (a pound of methyl bromide per 112 cubic feet of soil), a number of workers have tested it. Godfrey and Young (5) successfully employed a dosage of 2½ ml. per cubic foot, in gastight containers against nematodes and fungi. The writer killed large, damp sclerotia of *Sclerotinia sclerotiorum* buried 8 inches deep in outdoor piles of rather wet potting soil at a temperature of 53° F. with 2 pounds of methyl bromide to the cubic yard when covered with glue-coated paper. A dose of 1 pound was not quite sufficient in another test under similar temperature conditions when the sclerotia were dry at the time they were buried, but it did give good control of damping-off organisms.

Methyl bromide comes in 1-pound cans and in metal cylinders, and at ordinary temperatures, above 41° F., it is under several pounds pressure. Convenient dispensers have recently been devised which aid materially in handling it. In addition it can be dissolved in various other solvents of higher boiling points such as alcohol, xylol, ethylene dichloride, and carbon tetrachloride to enable it to be handled in open containers at ordinary temperatures. Much of the recent work on the control of nematodes and fungi has been done with such solutions (11). One composed of a 3-to-1 mixture of ethylene chloride and carbon tetrachloride plus 10 per cent methyl bromide is now marketed under the trade name "Dowfume G." Another containing 15 per cent methyl bromide in xylol is called "Iscobrome."

That methyl bromide solutions possess rapid penetrating power is indicated by a recent experiment performed by Lear. To a series of 1-gallon crocks of soil infested with a quantity of fresh, unrotted nematode galls, standard doses of Dowfume G (2 cc.) were added and the surface was sealed with 100 ml. of water. At the end of 2, 4, 12, 24, and 26 hours the galls were removed to crocks of fresh, nematode-free soil in which tomato seedlings were set. At the end of 6 weeks their roots were carefully examined. The mean number of galls per plant for the exposure periods just enumerated were but 2.3, 1.8, 3.5, 1.5, and 3.0 respectively whereas the checks had 207 galls, indicating that the fumigant had penetrated a few inches of soil and a half inch of tomato root in less than 2 hours. Godfrey and Young (5) have also drawn attention to the rapid penetration of methyl bromide into unrotted root galls. The advantage of this to a greenhouse grower whose crops must often follow in quick succession is considerable.

In another experiment performed by Stark and Lear in which the nematode

galls were allowed to undergo decay in crocks of soil for periods of 0, 4, 8, 12, 16, 20, and 24 days before treatment, the results showed that for the fumigant containing methyl bromide the period of rotting was of no importance, since test plants had galls to the number of 0.5, 0, 0, 0.8, 3.3, 2, and 0.3 for the periods of decay indicated. In the case of chloropicrin, however, galls on the test plants numbered 223, 100, 13, 177, 284, 12, and 0 respectively indicating that a period of delay before treatment is very important. The figures furthermore suggest that there is a period in the life cycle of the root-knot nematode when it is most resistant to chloropicrin. This period is believed to be the young larval stage just before it breaks out of the egg, particularly if covered with the protective secretion which the females sometimes provide.

Soil has been sown to beets 48 hours after treatment with methyl bromide fumigants and tomato plants have been set a week after treatment without loss. The optimum dosage rates found by Stark, Lear, and Newhall (11) for Dowfume G injected 4 inches deep on 10-inch centers in a tomato greenhouse lay between 4 and 6 ml. per injection, requiring 18 to 26 pounds per 1,000 square feet, at a cost of $2.88 to $4.20 or $120 to $180 an acre. They found that although more complete eradication of the root-knot nematode might be ensured with the higher dosage rate, nevertheless the yields of tomatoes were no better. Chickweed seemed to be controlled in one greenhouse by applications of 6 ml. per injection on 10-inch centers.

The fact that many growing plants tolerate methyl bromide at concentrations up to a pound per 1,000 cubic feet of air makes it possible to treat soil in part of a greenhouse with safety when plants are growing near by.

The results of recent tests with some soil fumigants in a tomato greenhouse in New York State where root-knot nematode was severe are given in table 4.

SOIL FUMIGATION HAZARDS

Mention has been made of the danger to living plants from fumes of chloropicrin escaping from soil in an adjacent part of a greenhouse. It may take two or three weeks to eliminate such materials as formaldehyde, DD mixture, and chloropicrin from the soil. Tetrachlorethane, ethylene dibromide, dichlorisopropyl ether, and dichlorethyl ether may be even more tenacious. Ethylene dichloride, xylene, carbon disulfide, and methyl bromide mixtures, on the other hand, are all less toxic or quicker to leave the soil and ordinarily permit sowing seed a week after treatment, provided soil temperatures are 65° F. or higher. Vapor pressures for these chemicals are given in table 5.

The hazards to the operator are those incident to the handling of any fumigant. He must avoid spilling them on his skin or clothing. Fire and sparks must be kept away from the vapors of carbon disulfide. Many fumigants cause considerable discomfort if breathed for long, and cyanide and methyl bromide may even be fatal. The bromide can cause numbness, blistering, and skin cracking some days after exposure under certain circumstances. Perspiration-soaked leather and rubber shoes or gloves are to be avoided.

For some fumigants the dangers may be incompletely known, and therefore

care should always be taken and manufacturers' directions followed closely. An abundance of fresh air during treatment periods in a greenhouse is advisable. The writer usually has a gas mask at hand, though he has never resorted to using it.

DEVICES FOR APPLYING SOIL FUMIGANTS

Since carbon disulfide was first employed by Thenard against the grape phylloxera nearly 75 years ago, a number of hand injectors have been developed. In

TABLE 4

Results of soil treatments for root-knot control in a greenhouse at Amsterdam, New York

TREATMENTS*	DOSAGE PER INJECTION†	MEAN NUMBER GALLS PER SQUASH PLANT IN 6 WEEKS	DEGREE OF INFECTION ON TOMATO ROOTS AFTER 4 MONTHS‡
	ml.		
1. Check..................................	0.0	47.9	3.30
2. Ethylene dichloride§....................	15.9	81.8	2.93
3. Chloropicrin§..........................	2.2	31.2	2.53
4. Dowfume G (10 per cent CH₃Br)........	3.4	11.7	1.27
5. Dowfume G (10 per cent CH₃Br)........	9.1	0.4	0.73
6. Dowfume G poured stream 3 inches deep‖.................................	7.0	3.5	0.52
7. Dowfume G poured stream 5 inches deep‖.................................	7.4	4.5	0.35
8. CH₃Br + ethylene dichloride (1–9).....	7.8	0.7	0.38
9. CH₃Br + propylene dichloride (1–9)....	7.6	1.6	0.46
10. CH₃Br + alcohol (1–9)..................	8.0	1.0	0.73
11. CH₃Br + xylol (1–9)....................	7.5	2.2	0.71
12. DD mixture............................	1.6	13.2	0.79
13. DD mixture............................	3.7	0.1	0.06

* Water seal applied with hose as soon as possible after plots were treated.

† All treatments except 6 and 7 injected on 10-inch centers. Plots replicated four times.

‡ Scoring system employed in which 0 means no infection, and 4, the maximum infection possible.

§ Treatments 2 and 3 may have failed because of large numbers of unrotted galls throughout the soil.

‖ Dosage is in milliliters per 10 inches of row, having been applied with a continuous flow two-row machine.

Europe, there were the McGowen, and the Spritzpfahl made by Carl Platz of Ludwigshafen, Germany; and the Vermorel Pal Injector made in France and sold for a time in the United States by P. E. Lirio of Vineland, New Jersey.

In this country progress has come chiefly in the last 15 years. A series of hand injectors were made in California by Stege, beginning with a Hand Prod Set, followed by the Economy Carbo-Injector and more recently by the Mack Fumigator Injector. The first two of these devices were little more than hollow pointed tubes forced into the ground, through which measured amounts of

liquid were allowed to flow by gravity. This was a slow process. It has been greatly speeded up in the Mack injector by including a force feed pump in the upper part of the prod which accurately measures and forcibly ejects the liquid with one stroke. This injector is suitable for use with a variety of volatile soil fumigants, as it can be calibrated to deliver from 1 to 60 ml. at a stroke.

TABLE 5

Pertinent physical characteristics, approximate dosages, costs, and effectiveness of some potential volatile soil nemacides

FUMIGANTS	BOILING POINTS	VAPOR PRES- SURE AT 25° C.	SP.GR.	VOL- UME PER LB. (AP- PROX.)	DOSAGE RATES*		COST OF MATERI- ALS		EFFECTIVE‡ CONTROL			PERIOD OF PER- SISTENCE§ IN SOIL
					Per 100 sq. in.	Per 1000 sq. ft.	Per lb.	Per 1000 sq. ft.	Ne- mas	Fungi	Weeds	
	°C.	mm.		ml.	ml.	lbs.						
1. Carbon di- sulfide.......	46.3	361.0	1.263	358	6.0	24.1	$.08	$1.92	good	vari- able	fair	short
2. Chloropicrin...	112.4	24.0	1.651	274	2.0	10.5	.80	8.40	good	good	fair	medium to long
3. DD mixture...	95–150	40.4	1.198‖	384	4.0	15.0	.15	2.25	good	poor	poor	long
4. Dichloriso- propyl ether.	187.1	....	1.113	413	2.0	7.0	.15	1.05	good	....	....	long
5. "Dowfume G"¶.........	43–85	4.7**	1.559	329	6.0	26.3	.20	5.26	good	fair	fair	very short
6. Ethylene di- bromide.....	131.7	12.0	2.170	212	1.0	6.8	.28	1.70	good	....	fair	long
7. Ethylene di- chloride.....	83.5	85.0	1.257	361	10.0	40.0	.08	3.20	good	poor	poor	short
8. Methyl bro- mide........	4.6	1824.0	1.732	262	0.6	3.3	.65	2.15	good	fair	fair	very short
9. "Isoco- brome"††....	....	....	.998	460	4.0	12.6	.35	4.42	good	fair	fair	very short
10. Pentachloro- ethane	160.5	4.0	1.681‖	274	9.6	50.0	.20	10.00	good	poor	poor	long
11. Tetrachloro- ethane.......	146.3	6.8	1.580	322	10.0	44.7	.19	8.49	good	poor	good	very long
12. Xylene........	138.8	10.0‖	.8668	532	8.0	21.6	.05	1.08	good	....	....	medium

* Dosages given are currently believed to be satisfactory for commercial root-knot nematode control in sandy soil at 70° F. when injected on 10-inch centers and if sealed in with water. A few of these materials probably do not need to be sealed in. The dose for ethylene dichloride may be too low.

† Prices are not all authorized and usually represent lowest available price in drum lots.

‡ Much variability in effectiveness may be expected under different conditions and for different pathogens; therefore ratings are tentative at best.

§ Usually a long period of persistence in the soil, 2 or more weeks, means considerable toxicity to subsequent plant growth, whereas a short period of a week or less denotes relatively little.

‖ At 20°.

¶ Contains 10 per cent methyl bromide in a 3-to-1 mixture of ethylene dichloride and carbon tetrachloride, by volume.

†† Contains 15 per cent methyl bromide and 85 per cent xylene, by volume.

** Pressure in pounds per square inch.

The Innis Speiden Company has been confronted with the problem of devising a hand injector (Larvajector) which would withstand the corrosive action of chloropicrin. They have developed three models in the last 10 years, the first employing a set of replaceable leather discs in the pump plunger, the second employing a metal bellows-type pump, and the third a plastic diaphragm pump.

FIG. 1. HAND-OPERATED FLUID INJECTORS

Left to right—Cali Spray gravity feed type; first Innis Speiden force feed plunger model; third Innis Speiden plastic diaphragm pump type; Mack plunger type force feed fluid injector.

These could all be calibrated to deliver small doses, up to 5 ml. Their availability has contributed greatly to the progress made during this decade in the use of volatile soil fumigants (see figure 1).

Neller and Allison (7) built a two-row continuous drip type of applicator for subsurface treatment of muck soil with chloropicrin or carbon disulfide. It was drawn by a tractor and discharged the liquid through two small orifices beneath the soil at a constant pressure maintained by a pump. In 1939 the writer employed a 5-gallon tank mounted on a walking tractor in the successful subsurface treatment of an acre of muckland with 1,600 pounds of ethylene dichloride for bulb-nematode control. The solution flowed by gravity through copper tubes mounted behind two cultivator teeth extending to a depth of 4 or 5 inches beneath the soil surface, as illustrated in figure 2.

In 1943 the Innis Speiden Company built a number of two-row machines operating on the gravity principle just described. The machines are powered
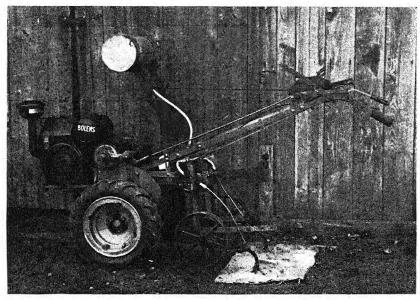
FIG. 2. CONTINUOUS FLOW, GRAVITY TYPE, TEMPORARY INSTALLATION MOUNTED ON GARDEN TRACTOR AT COST OF $12.50. USED ON MUCKLAND IN NEW YORK IN 1942

with small garden tractors. Essentially the fluid is valved into a pair of more or less vertical copper tubes so mounted 10 inches apart that they discharge about 3 inches beneath the soil surface. Packer wheels are mounted behind the delivery tubes to help compact the soil.

In the fall of 1943 the writer had a similar two-row gravity feed soil fumigator built but with a stand pipe added to reduce the pressure to a constant (see figure 3). For experimental purposes the design permits the release of the fluid at any depth to 5 inches, and the two delivery tubes can also be spaced 10, 15, or 18 inches apart.

A device for subsurface applications of soil fumigants on a large scale is the Stege, three-row, tractor-drawn Mechanical Subsoil Injector illustrated by Robbins, Crafts, and Raynor (10). It is pulled by a 30-horsepower crawler

tractor. Three delivery tubes, welded to the rear of a subsoil standard, discharge their fluid at the desired depth in a discontinuous stream. The flow is regulated by a measuring device at the top of each tube which is operated by a cam shaft arrangement powered by chains from the wheels. This device is said to treat several acres an hour. An entire 50-gallon drum of liquid fumigant can be mounted on the injector, and a rut filler and heavy roller are drawn behind to seal and compact the soil surface.

Carbon disulfide has been applied recently by spraying it under slight pressure directly on the ground immediately in front of a plow which turns the soil over on top of it.
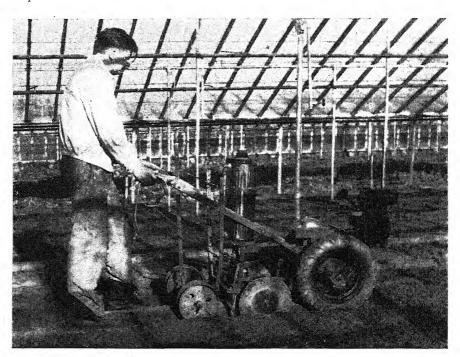
FIG. 3. TWO-ROW, GRAVITY TYPE CONTINUOUS FLOW INJECTOR EMPLOYED IN EXPERIMENTAL WORK IN NEW YORK IN 1943

DISCUSSION

There are many unsolved problems in this field of soil fumigation. No single chemical is as effective as steam, but several which control root-knot nematode nearly as well are less than one fourth as costly, and for commercial purposes this is good enough for many growers. The possibility of combining two or more fumigants to obtain higher efficiency has received but limited attention. Much treatment expense can be eliminated on widely spaced hill crops like watermelons by spot treatments of small areas where the seeds are to be sown, according to Taylor and McBeth (13).

The degree of adjustment that must be made in dosage rate when soils are

below 60° F. in temperature, or are too wet, or contain a high proportion of clay, needs more attention.

The writer has observed methyl bromide to fail where DD was a success in a sandy soil under conditions which pointed to an excessively loose condition of the soil as the probable cause. In some cases the nature of the subsoil must be considered in prescribing fumigants and dosages. A case of injury in the spring from chloropicrin applied the previous fall is on record in some of our metal-bounded field plots on shallow muckland over tough wet clay.

The maximum killing distances, k values, for some of the better fumigants need to be worked out under several soil conditions involving nematodes, fungi, and weed seeds. Dosage rates worked out for nematode control are seldom adequate where fungi are involved, as indicated in table 5, but raising the rate is sometimes effective and justifiable. Work on depth of injections is much needed with some nemacides.

If space permitted, something could be said about cyanamid, which has been used on the mucklands of Florida at 800 to 2,000 pounds per acre to control the celery pink-rot fungus *Sclerotinia sclerotiorum*. Urea should also be mentioned, since it is being used experimentally in the control of *Sclerotium rolfsii*, Granville wilt, Thielaviopsis, and weeds. The quantities of ammonia given off within two or three days after its application are believed responsible for the high pH usually attained and the disinfestation accomplished, sometimes by as little as 600 pounds in a neutral sandy soil. Further work will bring out the areas of usefulness of these compounds which are more or less toxic for a period after their application but which have an appeal from the standpoint of their ultimate fertility value.

SUMMARY

The need is stressed for a cheap method of eradicating pathogenic microorganisms, especially nematodes, from field soils, a need which promises to be met some day by the use of volatile fumigants injected beneath the surface.

The requirements of the ideal soil fumigant are outlined, and methods of testing are described.

Factors influencing the effectiveness of any given soil fumigant are discussed, with special reference to chloropicrin.

Data on the nemacidal efficiency of several better-known soil fumigants are given, including chloropicrin, carbon disulfide, DD mixture, ethylene dichloride, and methyl bromide.

The evolution of machinery designed for applying soil fumigants is outlined, and some of the unsolved problems in the field are mentioned.

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SOIL-STEAMING FOR DISEASE CONTROL

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Steaming and other means of heating the soil for the primary purpose of destroying soil-borne plant parasites is widely used in plant research and in the commercial culture of plants. Soil-infesting parasites, which invade the roots and stems of plants, although not so numerous in variety, nor so specialized in host relations, as those affecting aerial organs, are nevertheless an important group of pests. The serious nature of these parasites is due largely to the location of attack, namely, in the germinating seed and seedling stage of growth and on the roots; hence they often kill the plants or permanently retard their growth. These infected plant organs, furthermore, are less subject to rapid changes in environment which may check disease or to the practical application of effective control measures. The infested soil is also invariably a definite menace to succeeding crops of the same or other plant species. In addition to the true soil-infesting pathogens, a number of parasites of aerial organs may be harbored in or on the soil during certain periods of their life history.

The use of soil-steaming as a method of investigation in plant science and in the practical control of a variety of plant pests has increased steadily in recent decades. Wide variations in the methods and conditions of steam treatment, in the character of the soils treated, and in the plant species grown on steamed soil have yielded highly variable results, many of which are due directly to the effect of heat upon the soil itself rather than to influences on parasites. These secondary effects of heated soils need to be taken into consideration in drawing conclusions from results obtained in research and in practice.

The term "soil sterilization" is frequently applied incorrectly to the soil-steaming process. Soil sterilization implies destruction of all living organisms, together with the maintenance of this condition; whereas soil-steaming, heating, or chemical disinfection may accomplish only partial sterilization or pasteurization (4). Steaming is the most common method of applying heat to the soil; but since soil may be heated in other ways, as, for example, by dry heat, other methods of heating may be considered to fall under the category of steaming, since they usually depend upon converting the soil moisture into warm water or steam.

DEVELOPMENT OF METHODS

Surface-firing has been applied to soil from time immemorial for the purpose of improving conditions for plant growth. A part of this observed improvement was no doubt often due to disease control, even though not recognized as such. Technically, attempts to control plant disease by soil treatment were evidently

first made with chemicals. Kühn (16) in 1880 was perhaps the first to treat soil with heat for the specific purpose of investigating a plant disease organism, namely, the beet nematode (*Heterodera schachtii*).

The idea of applying steam to the soil as a practical control measure for a soil-infesting pest appears to have originated in 1893 in Illinois (21). The idea, along with the development of different methods of steam application, was adopted rapidly, particularly among growers of vegetables under glass in the states of Massachusetts (26), New York, and Ohio where glasshouse culture was already extensive before 1900 and where the nematode and other greenhouse pests were becoming increasingly harmful. The method was also soon adopted by growers of tobacco and other plants where close crowding of seedlings in plant beds often resulted in disease development, particularly damping-off. During this early period of soil-steaming, a large number of chemicals were tested as soil disinfectants, but none seemed to be so beneficial as soil-steaming, with the possible exception of the formaldehyde drench. Many efforts have consequently been made to lower the cost of steaming by improving the methods of application. More recently, attempts even have been made to heat soil for disease control by electricity (10, 19), by solar energy, and even through the heat of fermenting manure (7), but the older methods of soil-steaming have not been satisfactorily replaced.

DISEASES CONTROLLED BY STEAMING

Heat will destroy all forms of life, and it is largely the temperatures reached and the time of exposure to such temperatures that determine the death-point of organisms in the soil When the organisms to be killed are in a resting stage or in a dry condition, more heat may be required; but all plant pathogens are destroyed at relatively low temperatures, and such minor variations as exist are not usually taken into consideration in ordinary soil-steaming recommendations.

In some methods (sometimes referred to as "soil pasteurization") having the purpose of killing certain organisms with the minimum of effect on other organisms or on the soil itself, the thermal death-point of the organisms needs to be taken into consideration and the uniformity of heating must be assured. These methods, using temperatures as low as 60–80° C., are as yet chiefly of experimental value. In ordinary steaming practice, the temperatures in the soil are expected to reach approximately 100° C. for 20–30 minutes in layers of soil first exposed to heating and 60–80° C. in layers 6 to 12 inches removed from the exposure. The actual time of exposure may, of course, depend upon many circumstances. In the deeper layers of soil, killing temperatures may persist for many hours because of slow conduction of heat from the area; whereas the surface layers may cool rapidly after the treatment is discontinued. Plant pathogens and most other organisms are normally killed in 10-minute exposures at 60–70° C., or in 1 minute at 95–100° C. The virus of ordinary tobacco mosaic sometimes harbored in the soil is an exception, its destruction requiring exposure to 92° C. for 10 minutes. The practical problem is usually to reach all particles of the soil to be treated with such temperatures and exposures as are required. This necessitates periods of treatments far beyond those actually required for destruction.

Soil-steaming, as generally recommended, should be adequate to destroy all pathogens and other pests present and not merely specific organisms, as may sometimes be justified by chemical methods of soil disinfection. The diseases or other pests for the control of which steaming is not useful are naturally those which are commonly air-borne and which may quickly recontaminate the soil or infect the plants at any time from sources outside the steamed area. In this latter respect, nonvolatile chemical disinfection, because of its residual effect, possesses an advantage over steaming.

Little purpose would be served by listing the specific crop diseases that have been or may be controlled temporarily by soil-steaming. In practice, steaming has found its greatest application against stem and root diseases of plants grown in greenhouse flats, outdoor seedbeds, or nurseries, and in large glasshouse areas where the plants are grown under close or crowded conditions. The types of organisms most frequently concerned under such conditions are pathogenic fungi and nematodes, although the process may also be equally applicable to soil-borne bacterial pathogens and viruses. Certain insects and weeds should also be included in the category of pests controllable. Specific diseases for which steaming has been frequently used include damping-off (mostly *Pythium* and *Rhizoctonia*), root knot (*Heterodera radicicola*), root rots (*e.g., Thielaviopsis basicola*), and wilts (*e.g., Bacterium solanaceraum*). Except for recontamination, the control may, of course, be complete for such diseases, and the benefits often represent the difference between success or failure of seedling plants and crop production. Actual disease control is usually to be regarded as only temporary, ranging in time from about 6 weeks to 6 months. Steaming is consequently less useful in soils planted to susceptible plants for an entire season or over into the following year.

INFLUENCE OF STEAMING ON SOIL AND ON PLANT GROWTH

The net result of steamed soil on plant growth is determined by the combination of several beneficial and injurious influences which are produced by the process. The various influences of steaming may be briefly summarized as follows:

Destruction of living organisms in the soil, *i.e.,* normal and desirable soil flora and fauna as well as plant parasites and propagative organs of higher plants, especially weed seeds.

An immediate chemical action, *i.e.,* the partial decomposition of certain organic and inorganic materials, resulting in the formation of substances toxic to plants, such as excessive ammonia, together with the liberation of materials beneficial to plant growth.

Subsequent biochemical action, *i.e.,* modified ammonification, nitrification, nitrogen fixation, and denitrification.

Physical action, *i.e.,* modified absorptive capacity of the soil for water, gases, and salts; modified capillarity, concentration of the soil solution, colloidal state, mechanical condition, color, and odor.

Physiological action of these changes on the subsequent development of beneficial lower organisms and of green plants in these soils, *i.e.,* retardation or acceleration of lower organisms, seed germination, and plant growth.

Some of these influences of soil steaming are of particular interest in relation to disease control measures and are worthy of further consideration in this connection.

Growth of microorganisms in heated soils

The increased development of bacteria and fungi in reinoculated steamed soils, above that in unsteamed soils, has been repeatedly observed and demonstrated. Following the early work of Hiltner and Störmer (9), a large amount of literature has accumulated concerning the development of microorganisms in "sterilized" soils and the explanation of the observed behavior. One of the most controversial of these problems has centered around the phagocytic protozoan hypothesis of Russel and Hutchinson (22), which has been reviewed in detail by Kopeloff and Coleman (14). A good example of increased fungus growth on heated soil is that of *Pyronema confluens* Tul., which was first given detailed consideration by Kosaroff (15). Although it is evident that heated soils are rendered more favorable for the growth of some microorganisms than for others, it is generally agreed that most fungi and bacteria and perhaps other lower forms of plant and animal life find heated soil a distinctly more favorable medium for development than unheated soils or soils treated with chemical agents. Claims have been made in some instances that the introduction of pathogens into normal soil have failed to yield infection, whereas inoculation into steamed soils yielded excellent parasitism. It has frequently been noted that plants grown in steamed soil and subsequently naturally recontaminated with pathogens show unexpected high amounts of infection. Hartley (8) considers this behavior a disadvantage of sufficient importance from the standpoint of pine nursery beds to use it as an argument against the practical value of steaming soil for such nurseries. Edgerton (5) found the increased infection with the tomato Fusarium wilt on steamed reinoculated soils to be sufficiently great to warrant its use as an aid in eliminating susceptible strains in breeding for disease resistance. Similar evidence of increased infection on steamed reinoculated soils, as compared with unsteamed soils, has been noted by the writer with a number of other soil-infesting plant parasites. The damping-off of garden cress by *Pythium debaryanum* and of tobacco seedlings by *Rhizoctonia solani* may be especially rapid on reinfested sterilized soils. Flax planted in steamed and unsteamed soil, to which equal quantities of inoculum of *Fusarium lini* were added, showed decidedly more wilt in the inoculated steamed soil. Similar results were obtained with *Fusarium conglutinans*, *Fusarium oxysporum* var. *nicotianae*, and *Thielaviopsis basicola* for their respective hosts, cabbage and tobacco. A number of other investigators have reported similar results with other plant parasites.

The acceleration of growth of microorganisms in steamed soil is attributable in part to reduced competition with other organisms normally present in soil. Evidently it is also partly due to the increased concentration of the soil solution and accompanying nutrients formed. Some observers have suggested that the host plants are made more susceptible to disease by culture on steamed soil. In other instances, the virulence of the parasite itself is claimed to have been increased in steamed soil. These latter conditions may be more apparent than real.

It should be pointed out that increased infectivity by pathogens on steamed soil normally occurs only when the parasite is purposely reinoculated, and that this result should not be confused with the actual results obtainable in steaming

for disease control.   Although it frequently happens in practice that reinfested areas develop disease more readily in steamed than in unsteamed soils, these areas are usually relatively small and are usually due to improper steaming. Opportunity for such reinfestations may naturally be greatly reduced by careful attention to steaming and subsequent intelligent precautions to prevent accidental recontamination.

An increasing amount of attention is now being given to the ability of some soil fungi to inhibit or retard the development of soil-borne pathogens (13, 17, 23), but much remains to be done before this behavior can be put to practical use in steamed soils.

Retardation of plant growth on steamed soils

The steaming of soil is almost invariably accompanied by a temporary retardation of seed germination and early plant growth.   The extent of this injurious action, however, varies greatly with the soil type, the plant species grown, and the environmental conditions prevailing.   With many soils and plants, retardation may be almost imperceptible.   Often it can be recognized only by its effect on rate of seed germination.   With species that are especially tolerant to the toxic agent, increased rates of seed germination or plant growth may be apparent at the outset.   Some soils, however, are so productive of toxic substances when heated, and certain plants are so sensitive to these substances, that the beneficial results from disease control may be overshadowed.   Such responses are likely to lead to erroneous conclusions unless the temporary toxic action is considered and measures are taken for its prevention.   Unfortunately, there seems to be little correlation between the physical or chemical character of the soil and the degree of toxicity produced on steaming, and results cannot therefore be predicted readily.   Overheating of the soil, either through the temperature reached or the period of exposure to heating, is highly conducive to the toxin production, and such mistakes in treatment seem to be especially common in laboratory methods of steaming used in phytopathological research.

The Gramineae are, as a whole, tolerant to this toxic substance, whereas the Solanaceae and Leguminoseae are usually relatively intolerant (11).   The injurious action is most marked during the early stages of growth of the plants; or, more correctly, the soil gradually loses the toxic action, and in field practice recovery is usually prompt and rapid.   The time required for recovery, however, depends to a considerable degree upon the circumstances at hand, especially with respect to the reintroduction of normal soil flora and the existence of favorable environmental conditions for its activity.   Toxic soils stored sterile or dry, for example, may maintain the toxic property almost indefinitely.   That this toxic action is due largely to excessive ammonia, has been shown by the writer (11). Other harmful effects on plant growth may be attributable to other factors such as the physical effect of heating on the water relations of the soil (6).   The use of methods for hastening recovery and the advantage of delayed planting on steamed soils are often important in practice.

In addition to retardation in rate of plant growth, some heated soils may yield

striking symptoms of injury to roots and leaves, sometimes resulting in death of
the plants.   Leaf spots, vein necrosis with consequent leaf curling, stem lesions,
and discolored and lesioned root systems which are easily mistaken for pathogenic
infections may occasionally develop.   Tomatoes are especially subject to such
injuries, as are also tobacco, soybeans, and cowpeas.   It should again be empha-
sized that such injuries occur only when soils that are especially sensitive are
heated excessively and planted at once to species susceptible to the toxin formed.

The root injuries observed by the writer have been chiefly of four types,
namely: a fairly uniform yellowish brown discoloration of root cortex without
perceptible decay; transverse fissures in the cortex of small roots at close intervals,
accompanied by browning at site of wound; stunting of secondary or tertiary
rootlets and discoloration of root tips on penetration from parent root; and com-
plete decay of roots in late stages of injury in highly toxic soil.

The beneficial effects

Steaming or heating the soil results almost universally in a final striking bene-
ficial effect on plant growth.   When soil steaming is applied as a precautionary
measure against plant disease, the general improvement in vigor of plant growth
frequently leads to overestimation of the benefits derived from disease control.
The specific pests for which the treatment was planned may not have been present
or may have been less serious than anticipated because of weather or other
environmental conditions.   Increased supplies of plant nutrients may then be
largely responsible for the observed beneficial effects.   Other interpretations
have been suggested, such as that of "stimulation" of plant growth and destruc-
tion of "soil toxins," but these hypotheses have not found much support.

The increased plant food in steamed soil is attributable to two distinct causes,
namely, the immediate effect of heat, liberating nutrients from the organic and
mineral constituents present, and subsequent modifications resulting from in-
creased microbial activity.   The increased growth and healthy appearance of
plants on steamed soil is most frequently due to increased supplies of available
soil nitrogen, some of which no doubt arises from ammonia or ammonium com-
pounds previously inhibitory to the early plant growth on the same soil.

The improvement in earliness, uniformity, and vigor of plant growth as a
result of soil steaming is frequently so striking that the treatment is used chiefly
for this purpose in practical plant culture, although weed control is often regarded
as of equal importance in seedbeds.   The relegation of disease control to second-
ary importance often results in insufficient or improper steaming (*e.g.* treating
wet soils) and the recontamination of the soil through careless management.
Heavy disease injury may consequently occur on steamed soils during seasons
favorable for disease development.   The most beneficial results from steaming
are obtained when all factors concerned with the process are given attention
during the performance of the operation and in the subsequent management of
the treated soil.

METHODS OF STEAMING

The quantity or area of soil to be steamed may vary from a few soil pots or
soil flats for experimental purposes to large seedbeds or areas of several acres

under glasshouse culture. The type of equipment needed and the method of application may therefore vary greatly, although the principles involved may remain essentially the same in commercial practice, namely, heating all the soil to be treated to the necessary temperature for the required time at the lowest unit cost. Since steaming may cost as much as 2 cents a square foot, or $500–$1000 an acre, its adoption in commercial practice is naturally limited to crops that will warrant such an initial cost of production.

Steaming small quantities of soil in laboratories where steam sterilizers and autoclaves are available is a relatively simple process. The precaution should be taken not to place the soil in closed or tight containers which prevent the displacement of air by steam. Overheating should also be guarded against. Where manufactured equipment is not available and steam pressures of 20 or more pounds are at hand, various types of containers may be constructed of wood, metal, or concrete to confine the steam sufficiently for the purpose (12). In such equipment the soil is usually exposed in stacked soil flats that have been separated slightly to allow free circulation. On a somewhat larger scale, the soil itself may be placed on perforated steam pipes in an open box or bin, hence confining the steam to the soil. Many types of equipment for steaming have been described in this country and abroad, claiming special advantages for particular purposes (1, 2, 3, 12, 18, 20, 24, 25).

Where steam is not available, methods of "baking" under or over fires may be resorted to. These methods, for best results, depend upon converting the soil moisture into hot water or steam. Aside from "surface firing," various types and sizes of "ovens" have been designed for this purpose with fairly satisfactory results for small soil areas. These methods are, however, more likely to overheat parts of the soil while underheating other portions. Heating the soil by means of electricity has received some consideration in recent years, but experience has shown that the heating capacity of the equipment yet devised is not sufficient for quantities of soil such as are used in commercial culture (19). Other methods proposed for treating small quantities of soil, such as hot-water drenching, solar energy, and fermenting manure (7) also lack the capacity necessary to yield the rapid and reliable results required in the intensive commercial culture of special crops.

Large-scale steaming of soil is done principally by the buried perforated iron pipe or underground tile systems, or by the inverted-pan method. The perforated rake or harrow system has not been so generally adopted. The methods differ chiefly in that the steam is introduced into the soil either below or above the surface. In the underground systems, large areas may be steamed slowly; and in the inverted-pan systems, small areas are treated more rapidly. The former is usually permanently installed equipment, whereas the latter is portable. For details of installation and operation of such methods, other publications should be consulted (3, 12, 24). The most desirable system depends upon the circumstances at hand. All methods involve the problem of supplying a sufficient capacity of steam for the size of the entire area to be treated or for the quantity of soil steamed at one time. The steam should preferably be under considerable pressure in order to move it into the soil in a relatively "dry" condition. The

boiler capacity, the boiler pressure maintained, the size of the pipe or hose used, and the area or quantity of soil treated in one operation are consequently the chief factors to be considered in relation to obtaining the desired efficiency.

Satisfactory steaming also depends upon the rate of direct penetration of the steam into the soil and the subsequent conduction of the necessary heat to every particle of soil or living matter under treatment. Hence, the period of application required is determined by such circumstances as the volume or area treated at one time, the physical condition, and the moisture content of the soil. In actual practice, a part of the soil is overheated and a part may be underheated. The latter condition is especially likely to occur in large-scale disease control methods. The ideal soil sterilizer should permit loose, screened soil to pass through the steam instead of the steam to be forced into the soil, thus aiding uniform penetration of the steam and reducing the necessary time of exposure to steam temperatures. The efficiency of present methods of heating soil in terms of heat units required is undoubtedly low. It is not beyond the realm of possibility that engineering skills may eventually develop soil-heating equipment which may be applied at a cost within the practical limits of the culture of certain outdoor crops on a field scale. In instances where serious soil-borne diseases cannot be controlled by other means and where the general crop improvement is to be considered in addition to disease control, the need may develop the method.

SUMMARY

Soil-steaming is discussed with special reference to its bearing on phytopathological research and plant disease control problems. The limitations and advantages of the treatment are particularly emphasized, together with brief reference to the methods available for the purpose.
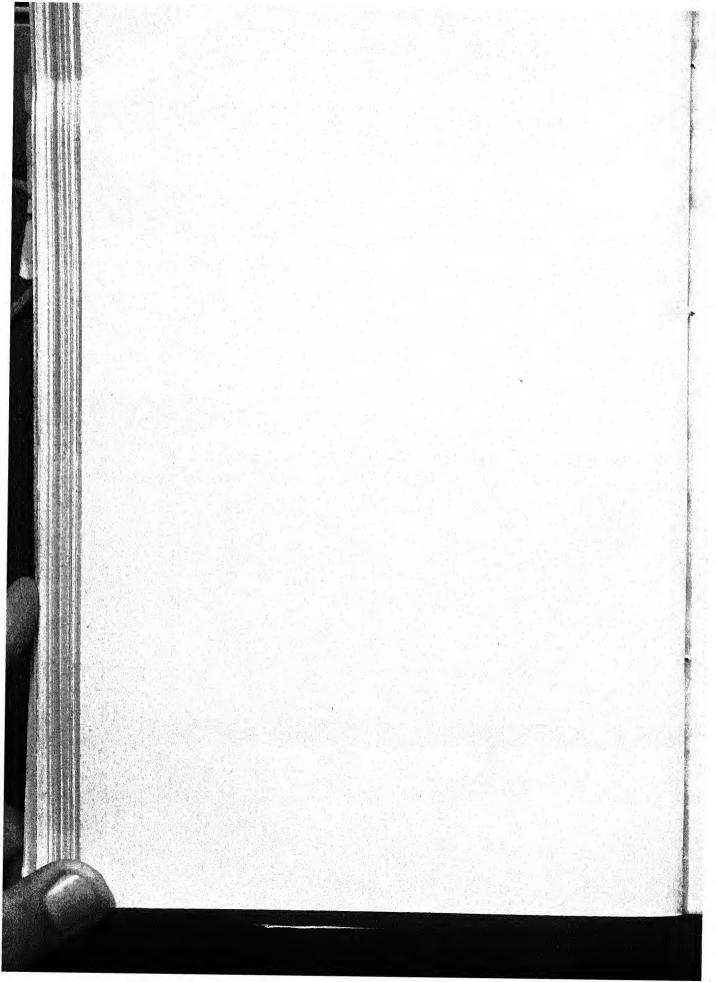
Although the chief object of steaming may be to destroy soil-borne disease organisms, many other desirable results are usually accomplished at the same time. These secondary effects often may be confused with the actual benefits derived from disease control. Conversely, retardation and other harmful effects on plant growth sometimes result which may lead to erroneous conclusions. Means for reducing such harmful effects are suggested.

The influence of steamed soil on the subsequent development of lower organisms, including plant pathogens, involves many factors which need to be taken into consideration in research studies as well as in practical control methods.

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SOIL FACTORS IN RELATION TO INCIDENCE AND SYMPTOM-EXPRESSION OF VIRUS DISEASES

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Early investigators including Mayer (18), Beijerinck (2), Ivanowski (8), and Clinton (3), regarded the soil as an important reservoir for the virus of tobacco mosaic, but with the accumulation of information on numerous hosts, and on the highly infectious nature of the virus, this view dropped from favor. In fact, the view was so unpopular in 1920 that the virus hypothesis for the etiology of the wheat rosette disease received very little consideration because the incidence of the malady was so definitely associated with the soil. However, there was a revival of interest in the soil when it became evident that wheat rosette is one manifestation of a virus mosaic.

At this writing, it is reasonably evident that very few plant-infecting viruses overseason in the soil. The outstanding example is found in the wheat-mosaic viruses associated with soils in certain localities in Illinois, Indiana, Virginia, and North Carolina (14) and in Japan (33). Oat mosaics observed recently in some of the Southeastern States are also induced by viruses that overseason in the soil. These viruses appear to be distinct from those infecting wheat.

Under certain conditions, the virus of tobacco mosaic overseasons in field soils, as shown by Johnson and Ogden (11) and by Lehman (12). Although relatively little experimental work has been done to determine the influence of edaphic factors on the expression of the virus diseases, it is known that nutritional factors do modify symptoms and with the tobacco-mosaic virus, nutrition is known to influence the amount of virus produced in the plant.

INCIDENCE OF VIRUS DISEASES IN RELATION TO SOIL FACTORS

Wheat-mosaic viruses

At least five species of virus cause mosaic in wheat and other small grains in the United States, but only one of these, *Marmor tritici* Holmes emend McKinney, is known to overseason in some manner in the soil (13, 14, 16). In the heavy silt soils and clay loam soils of Illinois and Indiana, the strains of virus comprising *M. tritici* (mosaic-rosette virus and yellow-mosaic virus) have been causing damage to the wheat crop in local areas since 1919. In the sandy soils of the Illinois River area in Illinois the disease occurs less frequently. In the Piedmont soils of the eastern coastal states these viruses have appeared only in limited areas. In Illinois, mosaic-rosette and yellow-mosaic viruses have shown the greatest increase in distribution.

That these viruses overseason in the soil is shown from tests conducted inside and outside the disease areas. The heavier soils in which mosaic wheat plants

have been growing, usually induce mosaic in wheat the following season when such soils have been transported into winter-wheat areas where the disease does not occur naturally.

When soil from the mosaic areas is drenched with a solution of formalin and water (1:49) the mosaic disease does not occur in wheat sown in the soil (13). Similar results are obtained when these soils are sterilized with steam.

Wheat plants grown in pails and in small plats containing disinfected soil and located in infested fields containing thousands of diseased plants remain mosaic-free throughout the entire crop season as long as the soils do not become contaminated with infested soil. Outside of the infested areas, wheat plants growing in noninfested soil have never shown signs of mosaic when located a few feet from diseased plants growing in soils from infested fields.

Manual inoculations have shown repeatedly that the virus is present in the mosaic leaves, yet no infection has yet been obtained in plants when grown in sterilized soil to which liberal quantities of mosaic leaf tissue were added 3 months previous to seeding. Also, wheat has remained mosaic-free when grown in pots containing the root and stubble debris from previous crops of mosaic plants that were infected by means of manual inoculations with juices from mosaic leaves. These observations make it appear that naturally infested soils contain some important contributing factor in addition to virus. It is possible that the virus overseasons in some soil-inhabiting organism that serves as a vector.[2]

Noninfested soils can be infested by sprinkling infested soil in the seed trenches, but the infection is enhanced when a 2- to 4-inch layer of infested soil is used. For routine testing, this layer is spread on the surface of the noninfested soil.

Studies conducted by Webb (34, 35) indicate that a $\frac{1}{2}$-inch layer of infested soil located at any level in a column of non infested soil 11 inches deep can induce some infection in wheat plants. Though Webb's data (35) are somewhat erratic, this may be accounted for on the basis that a $\frac{1}{2}$-inch layer contains too small a quantity of infested soil, since other of his tests show that a high rate of plant infection was favored when the containers were filled with the infested soil.

In Webb's experiments (35) infection was gradually reduced as infested soil was diluted with noninfested soil. With the particular lot of infested soil used in these tests, rosette and mosaic appeared in 5.3 per cent of the plants in soil diluted in 31 parts of noninfested soil. Dilution end points vary, depending on the initial degree of virus infestation.

From tests carried out with wheat-yellow mosaic in Japan, Ikata and Kawai (7) concluded that the virus enters the plant exclusively through the roots and root crowns, mostly at a soil depth of about 3 cm. and never below 15 cm.

Observations have indicated that sandy loam soils do not retain their infestation for as long periods as the heavy silt loam and clay loam soils. Infested sandy soils in the Illinois River drainage area have frequently manifested little or no sign of mosaic in susceptible wheat the season following a severe outbreak

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[2] In a previous statement (16, p. 323, col. 2, paragraph 2) the author inadvertently failed to mention the 3-month lapse between application of the tissue to the soil and the seeding.

of the disease. Heavy soils and sandy loam soils sometimes retain the infestation in field plats for at least 9 years, but sometimes such soils fail to induce the disease in appreciable quantity the second year.

In experiments conducted by Webb (35), infested silt loam soil from Illinois was placed over cloth in Büchner funnels and drenched with water, the drainage water being collected and allowed to stand until the silt particles settled out. After settling, the silt was recovered by decanting the clear water. Part of the water fraction was filtered through double paper filters. The silt fraction, the cheesecloth filtrate, and the paper filtrate were added to separate lots of steam-sterilized soil and to noninfested soils without sterilization. These amended soils and the original infested washed and nonwashed soils were tested for infestation by growing wheat. The net result was that the original infested soil induced just as much infection after having been washed as when not washed. In both soils 95–100 per cent of the plants were infected. There was no infection in the soils to which the cheesecloth filtrate was added, there was a trace of mosaic mottling in one pail to which the paper filtrate was added, and 25 per cent of the plants in the pails receiving the fine silt fraction developed rosette and mosaic. Similar tests were not carried out with infested sandy soils.

Ikata and Kawai (7) studied soil filtrates in Japan. They failed to obtain evidence of wheat-mosaic infection from filtrates.

Date-of-seeding tests (13, 34) show that the amount of infection gradually decreases with increasing lateness of fall seeding, and when seeds are sown in the infested soil so late that emergence is delayed until spring, the mosaic disease fails to appear. The mosaics under discussion have rarely appeared in spring-sown wheat, and when they have appeared, the spring weather continued cool for an unusually long time and very few plants were involved.

As shown by Webb (34) soil temperatures ranging from 10° to 16° C. with soil moisture at 52 per cent[3] favored infection, and subsequent tests (14) have shown that the typical field symptoms of rosette and mosaic can be duplicated in culture chambers the year around when the temperature of the chamber is maintained near 15.5°C. with 8 hours of sunlight daily. Temperatures up to 18.3°C. have been satisfactory for making routine tests. Results are less satisfactory when the sun is obstructed for prolonged periods.

Ikata and Kawai (7) regard 15°C. as the optimum soil temperature for the expression of yellow mosaic in wheat in Japan. They reported that fairly severe effects may occur at 10°C., whereas at 20°C. symptoms are inconspicuous, and at 25°C. they are imperceptible.

In transplanting tests from infested to noninfested soil, under favorable temperature conditions, Webb (34) found that virus infection in Currell wheat started before the seventh day after seeding, and the greatest amount of mosaic occurred in plants that had been in the infested soil for 28 days before transplanting. Very little or no infested soil adhered to the roots or crowns of the transplanted plants, as they were carefully washed and then surface-sterilized for 5

[3] This percentage is based on the water-holding capacity of the soil, which was 60 per cent.

minutes in a solution of HgCl$_2$ in water (1:1000). The rosette expression of mosaic in Harvest Queen wheat did not appear in plants until they had been exposed to the infested soil for 14 or more days.

Wheat seedlings and plants of different ages ranging from 1 to 6 weeks old were transplanted from noninfested to infested soil (34). In a single test, infection occurred in plants of all ages when transplantings were made under temperature conditions favorable for infection; however, the percentage of infected plants was somewhat higher among those ranging from 2 to 5 weeks old when they came in contact with the infested soil.

Tobacco-mosaic virus

The virus of tobacco mosaic, *Marmor tabaci* (Holmes ex Valleau) McKinney (15), has exceptional survival qualities under certain conditions, yet the amount of virus that actually overseasons in tobacco fields seems to be relatively small and to be confined largely to tissue residues from diseased plants (11, 12). The activity of the virus is greatly reduced when infested plant refuse is exposed to moist soils that have a sufficiently open texture for good aeration. In heavy water-logged soils and in dry soil the virus seems to have the best chances for surviving the winter in quantity.

Johnson and Ogden's experiments (11) leave little doubt that, in Wisconsin, seedbeds and fields littered with much infested refuse are more likely to show heavy infection in the succeeding crop than when no infested litter is present or when seedbeds are properly sterilized before seeding in the spring.

The comprehensive tests conducted by Lehman (12) in North Carolina indicate clearly that infested trash is a source of infection the following crop season in seedbeds and in fields. These studies substantiate the conclusions of Johnson and Ogden that the decomposition of the infested plant refuse favors low infection rates in the succeeding crop. It is concluded that by the proper use of the disc harrow and the plow, infested trash can be so thoroughly incorporated into the moist soil that the hazards of infection are greatly reduced the following season, and by avoiding tobacco and other susceptible crops for one crop season, the danger from trash is almost eliminated.

Tomato-mosaic and tomato-streak viruses

Doolittle (4) found that the tomato-mosaic and tomato-streak viruses live for at least 70 days in greenhouse soils. In the field, the mosaic virus will live 4 to 6 weeks in the soil. Tomato mosaic is caused by the same virus that causes tobacco mosaic, and the streak virus appears to be a strain of tobacco-mosaic virus.

Big vein of lettuce

Although big vein of lettuce has been studied for over 10 years, only recently have investigators transmitted it by means of aphids (31) and by manual inoculations of the foliar parts with extracts from the roots of diseased plants (5).

In 1934, Jagger and Chandler (9) reported that the causal agent is soil-borne

and that the amount of disease increases from year to year in favorable types of soil under constant lettuce culture in California. These studies indicated further that the disease is controlled when infested soil is partly sterilized with formaldehyde or with steam. The incidence of the disease was not influenced by manganese sulfate, zinc sulfate, boric acid, iron sulfate, copper sulfate, various commercial fertilizers, stable manure, or green cover crops applied to the infested soil. Furthermore, leaching infested soil with water did not reduce the amount of disease. In California and Arizona, the disease is more prevalent in heavy than in light soil. The soil-borne nature of the big-vein disease and the control by steam sterilization (3 hours at approximately 10 pounds) has been verified by Thompson, Doolittle and Smith (31) working with infested soil obtained from lettuce fields in the Eastern States. These investigators conclude that the causal agent will persist for at least 1 year under field conditions.

Pryor (19) found that the incidence of big vein increases with increasing soil moisture. He tested infested soils from the Imperial Valley and from Salinas, California, the data obtained from the Salinas soil being regarded as the more significant. In the Salinas soil, about 85 per cent of the plants developed big vein when the water content equaled 85 per cent of the moisture-holding capacity. At lower moisture contents, the incidence decreased, until only about 10 per cent of the plants were diseased in soil containing moisture equaling 35 per cent of the moisture-holding capacity. A few diseased plants occurred in soil containing only enough water to keep the lettuce plants alive.

Thompson and Doolittle (30) found that low growing temperatures (45° to 50°C. at night and 50° to 60°C. during the day) favor the expression of big vein. This is consistent with the observation that the disease is more evident in the fall and winter-grown lettuce in the Imperial Valley.

The big-vein virus appears to be distinct from the wheat-mosaic virus (*Marmor tritici*), as no infection has been obtained by the writer in Harvest Queen wheat grown in big-vein virus-infested soil supplied from California by D. E. Pryor.

INFLUENCE OF SOIL FACTORS ON ACTIVITY OF VIRUS IN PLANT AND ON PLANT REACTIONS

Considerable information has been obtained on the effects of temperature and light on the symptoms induced by viruses, but the amount of information relating to soil factors in this connection is relatively meager.

During seasons when soil moisture is low, wheat plants with mosaic have a lower survival rate than healthy plants. In field and in greenhouse culture mosaic-diseased plants in general tend to wilt sooner than healthy plants as soil moisture is reduced. This tendency is most noticeable in plants having the severe yellow mosaics.

In comparative studies of symptoms induced by viruses, the most satisfactory results are obtained when soil conditions and other factors favor essentially a normal development of the host plant. Mineral deficiencies induce disturbances in the chlorophyll that may complicate or be confused with symptoms by some of the viruses.

Mosaics tend to be most conspicuous when the nitrogen level in the soil is not too high. An excess of this element causes the yellow mosaics to resemble the light-green mosaics, and the latter may be almost, if not completely, obscured as a result of an increase in the chlorophyll content of the foliage. Selection for resistance to wheat mosaics in the field is facilitated at a moderate nitrogen level.

The view that succulent plants are more susceptible to viruses has been expressed by many investigators, and applications of nitrogen fertilizers have tended to support this conclusion.

The effects of fertilizers on the incidence and severity of virus diseases have been reported by Shultz and Folsom (22), Janssen (10), Quanjer (20), Ainsworth (1), Samuel and Bald (21), Volk (32) and others, but the most detailed studies on this problem have been reported in the several papers by Spencer.

Working with tobacco-mosaic virus and a yellow-mosaic strain, Spencer (23) found that the number of local lesions in leaves was greatest at nitrogen levels beyond those that induced maximum growth in the hosts. In later studies he (24) appraised the influence of phosphorus and potassium applications on the number of local lesions and found that the curves for the number of lesions and for the green weight of the plants tended to run parallel as the phosphorus was varied. With potassium, the number of lesions was reduced more rapidly than the green weight of the host plant as this element was increased, and the optimum for the number of lesions was reached slightly before that for the green weight of the host plant.

In studies with yellow mosaic in Turkish tobacco, Spencer (25) found that the incubation time was shortened when the nitrogen was either excessive or deficient in comparison with the more nearly optimal applications for the plant. The incubation time was shortened when phosphorus and potassium were absent or in moderate amounts in comparison with amounts that were in excess of the requirements of the plants.

On the contrary, the amount of common-mosaic virus in tobacco was found to increase directly with the amount of nitrogen applied, and the plants having the greatest amount of virus were distinctly stunted as a result of an excess of nitrogen (26). In a later paper, Spencer (27) concluded that the nitrogen-deficient diseased plant cannot synthesize normal proteins from nitrogen already utilized by the virus, and that the virus cannot utilize nitrogen tied up in the normal proteins, that the virus acts as a foreign protein, and that in nitrogen-deficient plants, the biological activity of the virus, per unit weight of virus protein, decreased more than 40 per cent. As a result of further studies (28) he concluded that the increased activity per unit weight of virus protein associated with the increased nitrogen supply in mosaic tobacco is due chiefly to an increased rate of virus multiplication in the high-nitrogen plants, and slightly, if at all, to an inactivation of part of the virus in the low-nitrogen plants. In a subsequent report (29), however, he modified this conclusion.

In 1942, Spencer (29) reported on the progressive development of common-mosaic virus in the inoculated mature leaves of tobacco plants, including comparisons with the systemic virus produced in the young leaves of these plants.

In plants receiving nitrogen throughout the test, the virus in the inoculated leaves continued to increase both in amount and in activity per unit of weight until the leaves became senile (after 20 days) when the activity dropped. In plants receiving no nitrogen after the tenth day following inoculation, the virus protein and the infectious activity per unit weight decreased, the activity decreasing earlier than did the virus protein. Calculations from sedimentation studies by means of the analytical ultracentrifuge indicated that the virus preparations from inoculated tobacco leaves contained a greater proportion of large virus particles 5 days after inoculation than they did 20 days after inoculation. If the large particles represent aggregates of minimal infectious units that gradually disperse, this phenomenon may explain the observation that a given weight of virus protein becomes more infectious per unit weight when the nitrogen supply is adequate. However, as pointed out by Spencer (29), the largest particles may not be chemically identical with the smaller, more infectious ones.

Chemical analyses by Martin (17) and by Hills (6) indicate that the protein content in the leaves of mosaic-resistant tobacco (T.I. 448A) is influenced very slightly by the small amount of virus present in infected plants. When the soil was maintained at a moderate nitrate level, the protein content of the infected leaves was slightly higher than normal, but when the nitrate level was low, the protein content was normal or slightly below normal. High protein content is undesirable in commercial tobacco, and from the data available, it appears that this factor is of little or no consequence in infected commercial tobaccos carrying the resistance of T.I. 448A, especially in the major tobacco areas in the southern United States, where low levels of nitrogen are maintained.

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SOIL FACTORS AFFECTING INCIDENCE OF ROOT KNOT

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Soil factors, physical, chemical, and biological, have a controlling influence on the occurrence and activity of the root-knot nematode, *Heterodera marioni* (Cornu) Goodey, especially when existing free in the soil as eggs or larvae, and also on its effects on plants. Temperature, moisture, sunlight, aeration, hydrogen-ion concentration, organic matter and biological control, and soil fertility are the primary factors discussed in this paper. Effects of the practices of flooding and fallow, and movement and distribution of the nematodes in relation to soil texture and other factors will also be considered.

TEMPERATURE

The optimal temperature range for the development of the root-knot nematode is about 20° to 30°C. (10, 19, 42). The most rapid development occurs at 27° (36). The range for the complete life cycle from infection through egg laying is from 14.5° to 31.5°; penetration of roots occurs from 12° to 35° (36). The lowest soil temperature at which the disease is likely to be serious is about 16° (10, 19, 42); advantage has been taken of this minimum in growing such crops as lettuce in greenhouses at about 13° (37). The highest temperature for the disease is near the maximum for the growth of many hosts.

Experiments with tobacco under controlled temperature conditions showed that at 19° the galls are large, whereas at 25° they are smaller, more numerous, and more mature in the same length of time. The effects of infection at 25° are more injurious to the host than at 19° (10).

The time required for the development of a nematode from a free-living larva to an egg-laying female is 80 days at 14½°, 16 days at 27°; development is retarded at temperatures above 27° (36). A rather constant number of effective heat units is required for development at various temperatures between the minimum and the optimum. For tomatoes in constant-temperature cultures, this value is from 6,500 to 8,000 hour-degrees above 10° for development from gall formation to egg laying (36). For beans in the field, a mean value of about 10,000 hour-degrees above 12° for a complete generation is recorded (34). The data indicate that the potential number of generations per year under the most favorable conditions is 10 or 12 (34). The generation time varies considerably, however, with different hosts (11).

Laboratory experiments with nematodes in water show that all larvae are killed at 40° in 2¼ hours, and at 43° in 8 minutes; eggs in masses are killed at 40° in 5 days, at 43° in 1 hour and 40 minutes; and at 48° in 7 minutes (18). These data check closely with the observation (27) that soil temperatures between 46.7° and 48.9° should be maintained for 10 minutes in order to kill eggs and larvae. Soil temperatures high enough to kill larvae, according to the aforementioned data (18), have been reported from Hawaii (17) and Florida

(20), to depths of ¼ inch and 1 inch, respectively. Killing temperatures at still greater depths have been reported from Texas.[1] On a hot day in May, soil temperatures were recorded as follows: first inch, 49°; second inch, 43½°; third inch, 41°. Godfrey interpreted these data to mean that there were no surviving nematodes in the upper 3 inches of soil.

Repeated freezing at 0° does not kill eggs or larvae, but −20° kills all stages in 2 hours. At low but not killing temperatures, larvae are well adapted to conserve their energy and live in a more or less quiescent state (37). Effects of low temperatures are discussed further in connection with distribution.

MOISTURE

Moisture plays only a small part in root-knot development as long as the water content of the soil is favorable to the growth of the host; under very dry or very wet conditions infection is reduced (4, 10, 19, 25).

Root-knot nematodes are highly sensitive to drying. A relative humidity of 50 per cent or less kills larvae within 4 minutes, eggs in masses within 2½ hours, and eggs protected by gall tissues within 2 days. A relative humidity of 90 per cent has been found to kill larvae within 30 minutes and eggs in masses within 9 hours, but three fourths of the eggs in gall tissues were still alive after 20 days' exposure (13).

Some of the applications of drying to root-knot control include exposure of roots on the soil surface to the effects of drying and of other factors (6, 15), and the disinfesting of tools and of small amounts of greenhouse soil by drying (27). The time required to rid soil of nematodes by air-drying depends on the initial moisture content of the soil, the conditions for drying, and the size and character of the infected roots present. With inoculum in the form of tomato galls, less than 2 weeks is required (19, 27). With inoculum in the form of woody pineapple roots, 16 weeks is required with stirring of the soil, and more than 20 weeks without stirring (14).

Although the root-knot nematode is killed by complete drying, normally only the uppermost layer of soil becomes dry enough to accomplish this result (39). The nematode may live in a soil that is apparently dry if, as commonly happens, the soil atmosphere below the dry surface layer is saturated with water vapor; this condition favors the long-continued survival of larvae, because they are not so active as to deplete their store of reserve energy (37).

Hatching of eggs proceeds slowly in soil with moisture slightly above the wilting percentage, and becomes more rapid with increasing moisture, until at slightly above the moisture equivalent it occurs as rapidly as in shallow water (25). Larvae become more active with increasing moisture (37). In high-ridge plantings of potatoes in Nevada and of tomatoes in California receiving frequent shallow irrigation, nematode activity was found to be restricted to the lower portions of the ridges, leaving the upper portions, watered only by capillary action, virtually free of infection (31). Field observations on potatoes in Oregon indicated that frequent irrigation gave greatly reduced tuber infection in infested

[1] By G. H. Godfrey in a letter to the writer dated November 28, 1944.

soil, as compared with less frequent irrigation, the results being attributed in this case to lower soil temperature. An experiment on frequency of irrigation, however, showed only slight reduction (16).

Other moisture relationships are mentioned in connection with flooding and fallow.

SUNLIGHT

Larvae are killed within 20 or 25 minutes by the ultraviolet in sunlight, depending on the intensity; and eggs in masses are killed within 5 hours. The combined effects of sunlight, including heat and drying, kill larvae within 2 minutes, and eggs in masses within 30 minutes (13). The effect of ultraviolet in the field is obviously limited to the surface of the soil.

AERATION

The importance of oxygen, carbon dioxide, and other soil gases in the development of root-knot nematodes has been suggested, but experimental data appear to be lacking. A crust on the soil is reported to favor long-continued survival of nematodes by reducing aeration (39).

HYDROGEN-ION CONCENTRATION

According to tests with Hawaiian soils having pH values from 4.0 to 8.5, no great difference in infection is manifest within this range. There is possibly a slight but unimportant reduction at pH 7.6 to 8.0 as compared with lower points (12).

Muck soils in Ohio containing a large admixture of marl or of clayey subsoil and having a pH value of 6.2 were observed to be infested, whereas closely adjacent areas at pH 5.3 were not infested. Acidification of the former with sulfur to pH 5.4 markedly reduced infection of onions; liming to pH 7.1 had little or no effect. The relative nemacidal value of sulfur and lime could not be evaluated in this experiment (42).

ORGANIC MATTER AND BIOLOGICAL CONTROL

The use of organic matter applied in various forms and in various ways to control nematodes has been reported.

Incorporation into the soil of 50 to 200 tons of chopped pineapple plants per acre gave progressively greater reduction in number of galls on indicator cowpeas up to the 150-ton rate. The fewest galls were observed after 1 month of decomposition, and the number increased after 5 months, indicating the action during decomposition of some factor other than death of larvae. Substitution of Para grass or cane sugar for pineapple gave a comparable response. The permanent reduction in nematode population was attributed to the increase in nematode-trapping and parasitizing fungi and predacious nematodes and mites (22, 23). The temporary benefit was probably explained by the attractiveness of fresh and decomposing plant tissues to larvae, as distinct from the destruction of nematodes by their natural enemies (24).

The occurrence of biological factors has received considerable attention, but their importance in nature and the possibilities of their exploitation for control of root knot have not been demonstrated.

Large applications of mixed peanut hay and pine straw (or oat straw) buried in the fall in deep furrows beneath tobacco rows gave reasonably effective root-knot control in the succeeding crop (7).

Mulching infested soil with various materials or watering plants with an infusion of the mulch material gave increased growth and in most instances reduced infection of test crops (40, 41). These results, however, have been attributed largely to improved soil moisture conditions and the plant-food constituents liberated from the decomposing organic matter (29).

SOIL FERTILITY

Crops infected with root knot have been reported as deficient in phosphorus despite an adequate supply in the soil for normal crop growth (28), and in nitrogen (26), although in the latter instance fertilization increased the nitrogen content of infected pineapple plants without improving their growth. A potassium fertilizer has been reported as helpful in protecting plants from nematode injury (37).

Heavy fertilization is widely practiced in connection with root-knot control, and may enable a profitable crop to be grown in spite of heavy infection. On this point, A. L. Taylor[2] said, "Some of my own observations have indicated that root-knot tolerance is connected with the ability of the plant to form new roots to take the place of those invaded by the nematode. Obviously, a well nourished plant is more able to do this than a poorly nourished one."

FLOODING

Flooding of soil is widely considered to control nematodes (4, 30, 35, 37, 38, 39), although reports are conflicting (1, 19, 27). Periods from 1 or 2 weeks (38) to 35 or 40 days (4) are recommended to give greatly decreased infestation.

Results of flooding in a long-term experiment (1) indicated that about 4 months of submergence killed all larvae. Eggs survived longer, but the nematode population was greatly reduced after 12 months. No nematodes were found after $22\frac{1}{2}$ months. Hence, to rid infested soil of nematodes by continuous flooding under these conditions would entail the loss of 2 years' crops.

Effects of flooding have been ascribed to exhaustion of the larvae, which is hastened by increased activity in water (1), and to preventing the growth of host plants (30). The latter does not apply, of course, to rice fields, which are kept under water for 2 to 4 months and are reported to be usually free of the root-knot nematode (4). Truck soils in Florida which are flooded or waterlogged for part of the year are usually comparatively free of root knot (39).

Alternate flooding and drying are sometimes practiced to control root knot (30). A fluctuating condition between a slight excess of moisture and air-dryness materially hastens the death of the nematodes except when they are

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[2] In a letter to the writer dated November 23, 1944.

protected within woody roots (14). High soil moisture hastens the rate of decay of tomato galls (19), which leaves eggs and larvae more exposed to adverse conditions.

<div align="center">FALLOW</div>

The practice of clean fallow by frequent plowing and other means has been found more or less effective for root-knot control, especially during hot and dry weather (2, 3, 6, 8, 15, 17, 20, 21, 33, 37). This may be accompanied by such sanitary practices as the removal of infected potato tubers (3) or drying on the soil surface of roots of tobacco (6) or beans (15). In the dry fallow method applicable under arid conditions, immune cover crops of grains or weeds may be used to deplete moisture from the soil and thus hasten drying (37). Another method of fallow makes use of poultry or livestock confined on an area for a year or two, leaving the soil virtually free of root-knot nematodes and weeds and also well fertilized (8, 37, 38).

The reduction in nematode population in the soil by fallowing is usually attributed to starvation in the absence of host plants, combined under suitable conditions with direct killing by heat (15, 17, 20), drying (15, 20, 37), and aeration (39).

A control method recommended as highly effective for truck fields in southern Texas consists of three plowings at intervals of 7 to 10 days in midsummer. At each plowing a deeper layer of soil is exposed to intense effects of heat and drying (15).

In warm weather some females may take enough nourishment from plants growing only 10 or 12 days to enable them to mature and form viable eggs. Weeds should therefore be destroyed within 10 days after they show above the ground in midsummer, but may be left for a longer time in cool weather (37).

Since larvae have survived for at least 40 weeks in a completely fallow soil (14), it is not to be expected that one season of fallow will eradicate root-knot nematodes from the soil, but rather that it may enable one or more successful crops to be grown. Two successive seasons of summer fallow are considered necessary to eradicate the nematodes from potato fields on Long Island (3).

An objection to clean fallow by frequent cultivation is the more or less rapid depletion of the soil fertility (2, 20, 39). For this reason, cover crops of immune or highly resistant plants have been recommended instead of clean fallow (2, 33, 39).

<div align="center">MOVEMENT AND DISTRIBUTION OF NEMATODES</div>

Soil texture is a factor in movement and distribution of root-knot nematodes. Porous sandy or loamy soils are especially favorable, because the larvae have greater freedom of movement than in heavy soils. Larvae are more readily attracted to roots in sand than in soil, and the explanation is suggested that adsorption of attractive root excretions by soil colloids reduces the intensity and extent of attraction (24). Better drainage has been mentioned as another probable explanation of greater activity in sandy soil (30). After nematodes become established within the root, soil texture has no direct effect on their development.

In comparison with other factors, soil texture is of minor importance, because there are reports of severe infestations in heavy soils (37).

A larva by its own activity can travel through sandy soil at the rate of about 1 cm. a day (6), or about 1 foot a month (39), and at least 2 feet during its active larval life (6). Other agencies, however, seem to be more important in the spread of nematode infestation than the movement of the nematode itself (6). Such agencies include the transport of soil, especially if wet or freshly plowed, by various means (3, 6, 8, 37, 39), and the use of manure contaminated with infected plant materials (3, 8). Soil dry enough to be wind-blown as dust does not seem likely to carry these nematodes (17).

Depth distribution depends largely on the depth of plant roots. Largest populations are usually found at depths of 24 inches or less, but considerable numbers have been found at depths from about 27 inches (3, 9, 27) to 5 feet (32), or even 6 to 8 feet on peach and fig roots in sandy soil (37). Movement to escape drought and frost has been suggested (8), but data on this point were not regarded as significant (9). Earthworm burrows, which have been traced to a depth of more than 40 inches in greenhouse soil, very likely harbor nematode eggs and larvae (27).

The geographical distribution of the root-knot nematode includes nearly every country in the world; in regions that are too cold for development in the field, the nematode may become destructive in greenhouses (37). No detailed summary of world distribution has been found in the literature, but according to G. Steiner,[3] "This nematode is well distributed throughout all the States. . . . The damage under northern conditions . . . is not very noticeable because the season is too short for the production of more than one or two . . . generations, but the winter temperature is certainly not a controlling factor of this nematode, at least of its northern race."

Evidence on freezing in relation to survival in the field is apparently conflicting. Winter conditions on Long Island do not eradicate the nematode from potato fields or reduce the infestation materially (3). On the other hand, 2 years of overwintering experiments in northern Indiana, with nematodes introduced on tomato seedlings from the south, produced no evidence that the nematodes are capable of surviving the winter in that locality (5). Moreover, G. H. Godfrey[4] has said, "I infested some soil very heavily with nematodes (strain from the South) in the fall, at Madison Wisconsin. That winter the soil froze to a depth of at least 18 inches. Next year there was not a trace of infestation left." Such apparently contradictory statements strongly suggest the existence of races having decidedly different low-temperature reactions.[5]

[3] In a letter to the writer dated October 13, 1944.

[4] In a letter to the writer dated November 28, 1944.

[5] A paper has been published recently which clearly establishes the existence of host races (J. R. Christie and F. E. Albin. Host-parasite relationships of the root-knot nematode, *Heterodera marioni*: I. The question of races. *Proc. Helminthol. Soc. Wash.* 11: 31–37, 1944). The probability of differences between races also in reaction to temperature, moisture, and climatic factors in general, is suggested by A. L. Taylor in a letter to the writer dated November 23, 1944.

DISCUSSION

Soil factors such as temperature and moisture, as they affect the incidence of root knot, have been investigated rather closely. The conflicting evidence regarding winter survival suggests, however, that studies of temperature and perhaps other factors should be elaborated, due consideration being given to the possibility that physiologic races may be involved.

Data on the depth distribution of root-knot nematodes and their rapid multiplication under favorable conditions show that eradication from field soils must entail a long time and considerable expense. Opportunities for reinfestation are abundant and not readily controlled. Therefore, control measures are to be sought which will effectively and economically minimize the losses incurred. Besides the cultural practices discussed herein, much work has been done with heat and chemical treatments and with trap-cropping and resistant crops. In the latter connection, the question of host races deserves careful consideration.

The effects of flooding deserve further study. Where flooding occurs naturally or may be accomplished artificially at reasonable cost, it appears to be a promising control method, the mechanism of which seems not to have been well explained. The effects of organic matter, applied as a mulch or incorporated into the soil, should also be studied further, from the standpoint of chemical as well as biological changes produced. In view of recent reports that nitrites are effective as soil treatments for nematode control and that they may occur in phytotoxic concentration in the presence of large amounts of organic matter or water or both, a study of nitrites is indicated in connection with flooding and organic matter applications. Other chemicals which may accumulate under similar circumstances should also be considered.

The attractiveness of fresh or decomposing plant material to larvae, as reported herein, opens a promising field for study, which may help to explain other results obtained with organic matter. The identification of the attractant or attractants would be of fundamental interest.

Early infection may be assumed to affect the growth of the plant more seriously than infection after the plant has become well established. Thus the time of planting or transplanting in relation to soil temperature may be an important factor, and soil treatments applied to hill or row, rather than broadcast, may be of value. It has been observed that there is often no clear negative correlation between amount of root-knot infection and growth of the crop, because root knot is only one of a complex of factors determining growth. Where good growth has been obtained in spite of heavy infection, the infestation remaining in the soil must be considered in relation to succeeding crops.
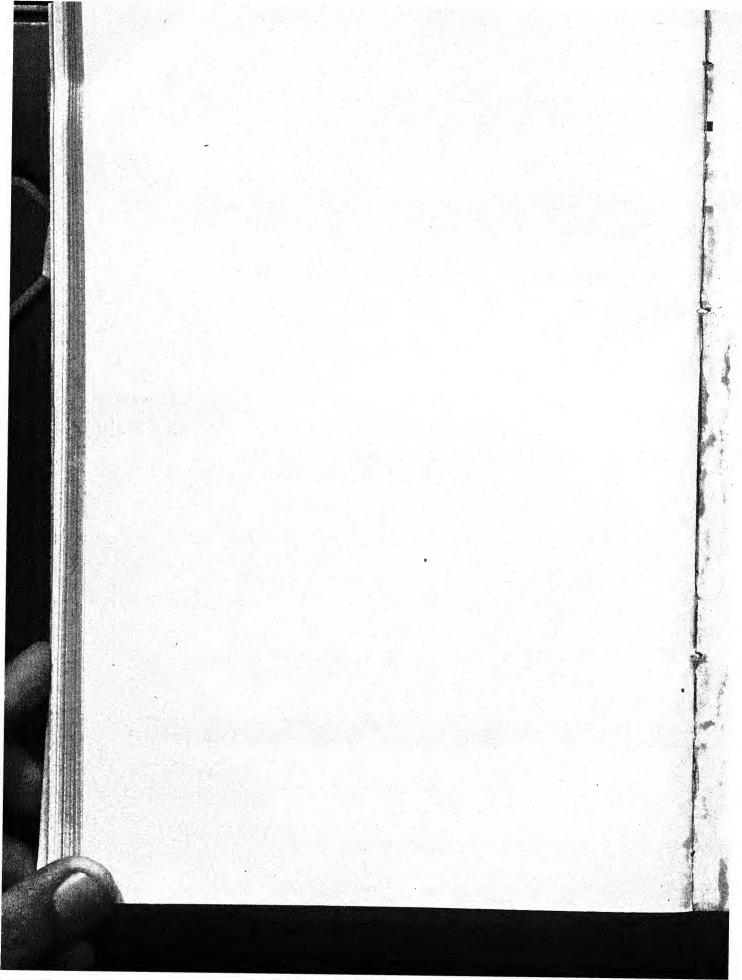
Studies of soil factors affecting incidence of root knot should include effects of other soil-borne pathogens, including the meadow nematode, *Pratylenchus pratensis* (de Man) Filipjev. This nematode, which has not been studied so thoroughly as the root-knot nematode, is probably affected by soil factors in somewhat the same way, and may produce similar symptoms in the portion of the host plant above ground. An experiment in progress at the North Florida

Experiment Station, on cigar-wrapper tobacco in 2-year rotation with native and crop plants, gives indication that the effects of these two nematode species are closely but perhaps not inseparably associated in the results obtained.

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PHOSPHATE ADSORPTION BY ILLINOIS SOILS[1]

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The reactions which soluble phosphates undergo and the forms which they assume in soils have been studied extensively.[2] Many investigators have been concerned with showing that phosphates are precipitated as some insoluble compound or, more recently, that they are adsorbed by the soil colloid. Although the later view is more generally favored at present, it is also recognized that a variety of reactions may occur; and modern colloid chemists (2, 7) recognize different types and degrees of adsorption, some of which are similar to precipitation reactions. This recognition that the same kinds of forces are acting in both adsorption and precipitation makes the necessity for distinguishing between the two types of reactions less important.

In working with Illinois soils, the writers found the adsorption concept the more applicable and the more adequate one to describe the reaction which takes place between soils and phosphate. Bray and Dickman (1) used this adsorption concept in setting up a tentative procedure for fractionating the inorganic soil phosphates based on fluoride replacement (6), and they have already outlined some of the ideas which soil chemists at Illinois have found useful in explaining the behavior of phosphates in soils. These ideas are based on the data presented by these workers as well as on data reported here for the first time. In interpreting these data the works of Davis (3), Scarseth (13), Murphy (10), Toth (14), Prescott (9), Russell (12), Ravikovitch (11), and others were freely consulted.

EXPERIMENTAL

The phosphate adsorption curve

That the reaction between soluble phosphate and Illinois surface soils has many characteristics of adsorption was demonstrated by the following procedure:

A series of tubes each containing 50 ml. of phosphate (Na$_2$HPO$_4$) solution of known concentration were shaken for 5 hours with 2 gm. of soil. After standing an additional 19 hours the suspension was centrifuged and the phosphate still in solution was determined by the method of Dickman and Bray (5). The amount of phosphate retained by the soil, that is, adsorbed, was determined from the difference in concentration between the added and the recovered solution.

Data obtained in this manner with Muscatine silt loam from the check plot of the Kewanee Experiment field showed that the phosphate adsorbed by the

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[2] For reviews of this subject, see Weiser (16) and Murphy (10).

soil increased with the concentration of phosphate in solution and that the amount adsorbed gradually approached a level above which there was little further adsorption regardless of increases in concentration.

Effect of soluble salts on phosphate adsorption

In an attempt to obtain clean separations more quickly in the centrifuge, a series of determinations was made in which the phosphate was added to a solution which contained 2 per cent potassium chloride. The assumption here was that this electrolyte would act as a coagulating agent without influencing the reaction between the phosphate and the soil. That this assumption was incor-
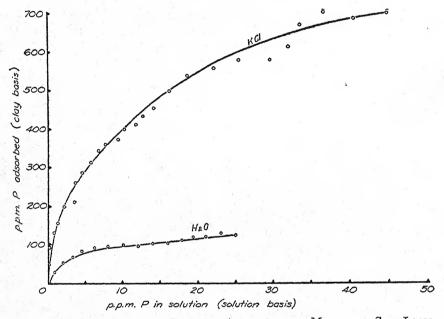
FIG. 1. EFFECT OF KCl ON PHOSPHATE ADSORPTION BY MUSCATINE SILT LOAM

rect is shown graphically in figure 1, where the phosphate adsorbed by the soil is plotted against the concentration of phosphate in solution at the end of the trial. From this graph it can be seen that typical adsorption curves are obtained both with and without potassium chloride, but that the adsorption in the presence of the potassium chloride is much greater. It was found that the phosphate adsorbed in the presence of KCl could all be removed by a series of extractions with KCl solution.

Effect of soil-solution ratio

In order to show that the type of adsorption curves just described was not dependent upon the limited conditions under which they were obtained, another experiment was carried out in which the soil-solution ratio as well as the concentration of phosphate in solution was varied. Except for these differences in

ratio, the technic was not changed. The phosphate was added as standard solutions of KH_2PO_4 and the final pH varied from 4.5 to 5.8 as determined by the Beckman glass electrode.

The data obtained from three different ratios again showed that the amount of adsorption was a function of concentration of phosphate in solution. If the phosphate adsorbed by the soil is plotted on a logarithmic scale against the logarithm of the concentration of phosphate remaining in solution, a straight line (fig. 2) is obtained for a considerable range of concentrations for all three
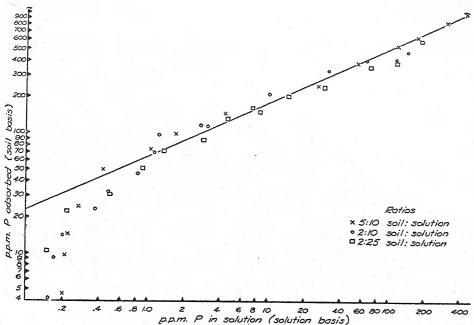
FIG. 2. ADSORPTION OF PHOSPHATE AT DIFFERENT SOIL:SOLUTION RATIOS BY MUSCATINE SILT LOAM

soil-solution ratios. Within this concentration range the extent of the reaction is well expressed by the equation of the line.

$$\log Pa = \log 63.1 + 0.44 \log Ps$$

where Pa represents parts per million of phosphorus (as phosphate) adsorbed and Ps is parts per million of phosphorus in solution. This equation can also be written in the more familiar form of the Freundlich equation, $a/m = KC^n$, where a/m represents the amount of material adsorbed per given weight of adsorbent, C is the concentration in solution at equilibrium, and K and n are constants.

The fact that the adsorption in the lower concentration ranges did not occur according to the equation is not to be interpreted to mean that the reaction is not one of adsorption. Although the Freundlich relationship was formerly used

as a criterion of adsorption, it is now recognized that his equation may hold only in limited ranges and that it is not applicable to all adsorption reactions.

It is difficult to understand how the data could be explained on the basis of the formation of a phosphate compound, or even a series of compounds, and it is not apparent how such an interpretation would be justified. The difficulties involved in applying solubility principles are evident, since there were no definite values for the solubility of the phosphate retained by the soil. The relative concentration of phosphate in solution and of that adsorbed on the soil was changed, but the phosphate concentration still determined the amount of adsorption, and the change was not stepwise.
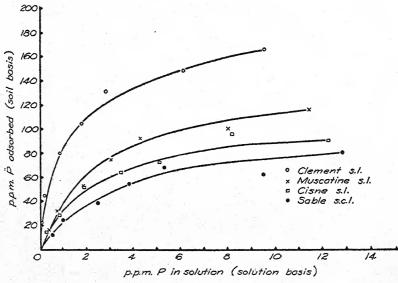
FIG. 3. ADSORPTION OF PHOSPHATE BY CLEMENT, MUSCATINE, AND CISNE SILT LOAMS AND BY SABLE SILTY CLAY LOAM

Adsorption by different soils

The ability of different Illinois soils to adsorb phosphate under the conditions described was compared. Samples used in this experiment were from the unfertilized plots of the Elizabethtown, Toledo, Kewanee, and Hartsburg experiment fields where the soil types in the order named are Clement, Cisne, and Muscatine silt loams, and Sable silty clay loam. The Sable and the Cisne represent, respectively, the youngest and the most mature members of the Illinois maturity series. The Muscatine represents stage II (next to youngest) and occurs widely in Illinois. The Elizabethtown field is in the extreme southern part of Illinois and is presumed to be representative of the rolling land of this unglaciated area. The Elizabethtown field gives large responses to phosphate fertilization, whereas the Hartsburg field responses are small. The four soils are all loess-derived and their colloidal clays are largely montmorillonite (beidellite) and illite clay

minerals.   Kaolinitic minerals may also be present in minor amounts.   The pH values of the samples in 1:1 suspensions are Clement 5.3, Cisne 4.8, Muscatine 5.1, and Sable 6.0.   The procedure and the technic were as described except that the phosphate was added as KH_2PO_4 that had been neutralized with potassium hydoxde

The data in figure 3 show that the Clement soil in general retained about twice as much phosphate as the Sable at the same concentration, whereas the Muscatine and Cisne soils were intermediate in the amounts of phosphate retained. This variation in the abilities of the different soils to retain phosphate was not great when it is considered that they represent an extremely wide range in soil type.   It is considered more significant that the curves were, in all cases, similar to one another and to those already described.

TABLE 1

Amount of phosphate adsorbed by Muscatine silt loam during different time intervals

PHOSPHORUS* (P) ADDED IN SOLUTION	TIME INTERVALS	PHOSPHORUS (P) REMAINING IN SOLUTION	PHOSPHORUS (P) ADSORBED BY SOIL (SOIL BASIS)†
p.p.m.		*p.p.m.*	*p.p.m.*
6	15 Minutes	4.2	45
6	1 Hour	3.7	57
6	1 Day	3.2	70
6	1 Week	2.3	89
6	11 Weeks	0.8	130

* Added as KH_2PO_4 + KOH.
† Soil:solution ratio = 2:50.

Effect of time on phosphate adsorption

To study the effect of time on phosphate retention, the same amount of phosphate was added to samples of Muscatine soil and the phosphate adsorbed was determined at intervals up to 78 days.   The phosphate was added as a standard solution of potassium phosphate that contained 1 per cent by volume of 40 per cent formalin and sufficient potassium hydroxide to adjust the solution to pH 7.0.   The data in table 1 show that the reaction was not complete after any particular time interval but that the rate of reaction did decrease.

Effect of time on solubility of added phosphate

In order to investigate the status of phosphate that has been in contact with the soil for different time periods, phosphate additions were made to samples of three different Illinois surface soils and the phosphate fractions determined after different time intervals.   For this experiment 2-gm. samples of the soils were weighed into small bottles and 2 ml. of water containing the appropriate concentration of phosphate as KH_2PO_4 was added.   A few drops of both toluene and ether were added and the bottles sealed and stored in the dark at room temperature.

At the end of each interval each sample was washed from the storage bottle with 50 ml. of water and placed on the shaking machine for 1 hour. The suspension was then centrifuged, the clear solution removed, and the phosphate determined. Three or four of these water extractions were made in succession. The sample was then leached with 100 ml. of N NH$_4$Cl, then transferred to a

TABLE 2

Added phosphate in different water extracts after different time periods

PERIOD OF SOIL AND PHOSPHATE CONTACT	ADDED PHOSPHORUS IN WATER EXTRACTS				TOTAL OF WATER-SOLU-BLE EXTRACTS	ORIGINAL PHOSPHORUS ADDITION
	1	2	3	4		
	p.p.m.	*p.p.m.*	*p.p.m.*	*p.p.m.*	*p.p.m.*	*p.p.m.*
Muscatine samples						
10 min.	20	8	5	4	37	50
45 days	5	4	4	5	18	50
3 years	1	1	1	. . .	3	50
10 min.	106	29	12	9	156	200
45 days	32	20	15	13	80	200
3 years	6	7	4	5	22	200
10 min.	1,078	154	62	34	1,328	1,500
45 days	463	138	105	87	793	1,500
3 years	73	43	33	33	182	1,500
10 min.	2,398	253	98	50	2,799	3,000
45 days	1,229	218		196	1,643	3,000
3 years	170	120	99	94	483	3,000
Cisne samples						
10 min.	23	7	4	3	37	50
35 days	4	3	2	3	12	50
90 days	4	4	2	. . .	10	50
3 years	2	2	1	. . .	5	50
10 min.	125	24	10	6	165	200
35 days	32	17	14	11	74	200
90 days	31	17	14	. . .	62	200
3 years	18	8	5	. . .	31	200
10 min.	1,169	116	39	18	1,342	1,500
35 days	713	130	86	57	986	1,500
90 days	679	137	93	. . .	909	1,500
3 years	224	92	. . .	. . .	. . . . .	1,500
10 min.	2,478	173	53	25	2,729	3,000
35 days	1,788	242	131	80	2,241	3,000
90 days	1,749	254	143	. . .	2,146	3,000
3 years	808	186	129	. . .	1,123	3,000

TABLE 2—*Continued*

PERIOD OF SOIL AND PHOSPHATE CONTACT	ADDED PHOSPHORUS IN WATER EXTRACTS				TOTAL OF WATER-SOLU-BLE EXTRACTS	ORIGINAL PHOSPHORUS ADDITION
	1	2	3	4		
	p.p.m.	*p.p.m.*	*p.p.m.*	*p.p.m.*	*p.p.m.*	*p.p.m.*
Clement samples						
10 min.	11	5	4	3	23	50
39 days	2	4	4	...	10	50
3 years	0	0	...	...	0	50
10 min.	99	24	12	7	142	200
39 days	24	18	12	12	66	200
3 years	12	8	...	...	20	200
10 min.	1,154	125	49	22	1,350	1,500
39 days	590	150	94	68	902	1,500
3 years	96	73	40	...	209	1,500
10 min.	2,424	224	74	43	2,765	3,000
39 days	1,560	285	168	106	2,119	3,000
3 years	587	195	132	...	914	3,000

flask with 100 ml. of neutral, N NH_4F and placed on the shaking machine for 1 hour. This procedure, according to Bray (1), determines the total adsorbed phosphate. After this fluoride extract was removed by filtration on a Büchner funnel, the easily acid-soluble fraction was determined.

For the easily acid-soluble determination, the samples were transferred to flasks with 400 ml. of Truog's reagent (15) [0.002 N H_2SO_4 buffered to pH 3 with $(NH_4)_2SO$] and placed on the shaking machine for 1 hour. Solid ammonium fluoride was then added to make the solution 0.5 N with respect to fluoride. After another half hour on the shaking machine, the samples were filtered and phosphate was determined in the filtrate. Organic phosphorus in the residue and in the extracts was determined at this point in the procedure, but these values are not reported, since the amount of phosphorus in this form did not change during storage. Fluoride interference in the phosphate determination was eliminated by the boric acid procedure (8). The fractionation carried out on these samples corresponds closely with that described by Bray and Dickman (1).

The phosphate removed from these stored samples by the successive water extractions is given in table 2. If it should be assumed that the water-soluble form were the only one which is usable by the plants, it is seen that even by this extremely conservative standard much of the added phosphate is recoverable after 3 years. In this connection it should be pointed out that the values given in table 2 do not represent all the phosphate which could have been removed by water. It is evident from the data that the samples which had received large applications were still giving up large amounts of phosphate when the extractions were discontinued. The number of successive water extractions that could be

made on a sample was limited because the sample became so dispersed that separation of soil and solution was practically impossible after three of four extractions.

The distribution of the added phosphate among the different fractions after different time periods is given in table 3. These values were obtained by sub-

TABLE 3

Added phosphate in the various fractions after different time periods

PERIOD OF SOIL AND PHOS-PHATE CONTACT	ADDED PHOPHORUS RECOVERED IN THE			TOTAL AMOUNT OF ADDED PHOS-PHORUS RECOVERED	ORIGINAL PHOSPHORUS ADDITION
	H_2O extract	NH_4F extract	NH_4F+ acid extract		
	p.p.m.	*p.p.m.*	*p.p.m.*	*p.p.m.*	*p.p.m.*
Muscatine samples					
10 min.	37	8	3	48	50
45 days	18	24	10	52	50
3 years	3	43	26	72	50
10 min.	156	23	7	186	200
45 days	80	101	26	207	200
3 years	22	97	39	158	200
10 min.	1,328	74	15	1,420	1,500
45 days	793	563	87	1,440	1,500
3 years	182	992	266	1,440	1,500
10 min.	2,799	108	19	2,930	3,000
45 days	1,643	1,231	131	3,000	3,000
3 years	483	1,924	480	2,890	3,000
Cisne samples					
10 min.	37	9	6	52	50
35 days	12	26	−3	35	50
90 days	10	27	4	41	50
3 years	5	34	13	52	50
10 min.	165	21	7	193	200
35 days	74	89	4	167	200
90 days	62	102	14	178	200
3 years	31	126	27	184	200
10 min.	1,342	55	12	1,410	1,500
35 days	986	369	33	1,390	1,500
90 days	909	441	49	1,400	1,500
3 years	...	...	...	...	1,500
10 min.	2,729	73	16	2,820	3,000
35 days	2,241	507	47	2,800	3,000
90 days	2,146	675	80	2,900	3,000
3 years	1,123	1,552	241	2,920	3,000

TABLE 3—*Continued*

PERIOD OF SOIL AND PHOSPHATE CONTACT	ADDED PHOSPHORUS RECOVERED IN THE			TOTAL AMOUNT OF ADDED PHOSPHORUS RECOVERED	ORIGINAL PHOSPHORUS ADDITION
	H$_2$O extract	NH$_4$F extract	NH$_4$F + acid extract		
	p.p.m.	*p.p.m.*	*p.p.m.*	*p.p.m.*	*p.p.m.*
Clement samples					
10 min.	23	9	20	52	50
39 days	10	20	12	42	50
3 years	0	12	3	15	50
10 min.	142	26	35	203	200
39 days	66	78	27	171	200
3 years	20	...	...	....	200
10 min.	1,350	58	42	1,450	1,500
39 days	902	409	83	1,390	1,500
3 years	209	948	195	1,350	1,500
10 min.	2,765	77	41	2,880	3,000
39 days	2,119	662	118	2,900	3,000
3 years	914	1,589	245	2,750	3,000

tracting from the determined value the amount of phosphate in the similar fraction of a sample to which no phosphate had been added. For completeness of the data, the amounts of phosphate in these check samples are given in table 4.

From the data in table 3, it is apparent that the water-solubility of the added phosphate decreased with time and that the reaction by which phosphate was removed from solution was not complete after any certain time period. At the end of 3 years, a significant portion of the original phosphate addition was still removable by three to four water extractions. This portion ranged from 10 to 30 per cent where smaller to larger applications were made. It is noteworthy that even the small phosphate additions increased tremendously the phosphate which the soil could supply to the solution.

Also evident in table 3 is the fact that nearly all of the added phosphate which was not recovered in the water-soluble fraction was found in the adsorbed fraction. Table 3 shows in addition that the conversion of the added phosphate into the acid-soluble form proceeded slowly. In parts per million this conversion was not great, but made up from 50 per cent of the total amount where the phosphate additions were small to about 5 per cent where the additions were large.

When the 1 N fluoride extraction was proposed by Bray (6) as a measure of the adsorbed form, it was believed that this fraction could be readily utilized by plants. It was also believed that the acid-soluble fraction could be utilized by plants but at a slower rate. If these hypotheses are correct, the high recovery of the added phosphate shows that little of the phosphate could be considered "fixed" in the sense that it would not be recoverable by plants. The fluoride extraction is possibly more vigorous than was originally supposed, but the fact

that the added phosphate remained in forms that were *more soluble than those native to the soil* would indicate little "fixation." This is emphasized when it is considered that the native phosphorus, especially in the Muscatine soil, is soluble enough for a better than average crop.

TABLE 4

Phosphate in the different fractions in the check samples

PHOSPHORUS ADDED	PERIOD OF CONTACT OF SOIL AND PHOSPHATE	PHOSPHORUS IN THE			TOTAL PHOSPHORUS REMOVED
		H₂O extracts	NH₄F extracts	NH₄F + acid extract	
p.p.m.		*p.p.m.*	*p.p.m.*	*p.p.m.*	*p.p.m.*
		Muscatine samples			
0	10 min.	6	24	35	65
0	45 days	4	27	30	61
0	3 years	7	28	36	71
		Cisne samples			
0	10 min.	5	21	19	45
0	35 days	6	24	29	59
0	90 days	4	22	26	52
0	3 years	5	32	32	69
		Clement samples			
0	10 min.	2	16	26	44
0	39 days	3	15	26	44
0	3 years	2	20	53	75

Replacement of adsorbed phosphate by other anions

The idea that phosphate is held in an adsorbed condition suggests the possibility of replacement by other anions. The ability of other anions to remove adsorbed phosphate was compared by making extractions with solutions of different salts. The soil used in this study had been prepared by adding K_2HPO_4 equivalent to 790 p.p.m. of phosphorus to a sample of surface soil from the untreated plot of the Toledo experiment field. The sample was sealed and stored in the dark at 20 per cent moisture for 5 years. At this time a weighed portion (equivalent to 1 gm. on the air-dry basis) was washed onto a Büchner funnel and leached with suction with 50 ml. of N NH_4Cl. This was followed by two successive 50-ml. leachings with a neutral solution of the anion to be studied. The same sample of soil was then placed on the shaking machine for 1 hour with another 50 ml. of the same extracting solution and again filtered. The phosphate was determined in each of the three extracts after appropriate measures had been taken to eliminate interference by the anion of the salt used. The amounts of phosphate removed by the different solutions is shown in table 5. The chloride, sulfate, thiocyanate, acetate, and borate ions have low replacing ability

and remove amounts which are similar to or smaller than the amounts removed by water alone. On the other hand the bicarbonate, citrate, oxalate, and fluoride ions are much stronger. The fluoride ion is outstanding in the ease and rapidity with which it replaces phosphate.

The fluoride ion, which has a relatively small radius, forms stable complexes with iron, aluminum, and silicon ions and is isomorphous with the phosphate ion in numerous compounds. The oxalate and citrate form complexes of considerable stability with iron and aluminum. The thiocyanate-iron complex and the chloride complexes with both iron and aluminum are known but are not highly stable. It may be postulated, therefore, that the replacing abilities are related to the tendency of the different ions, in comparison with phosphate, to form stable complexes with ions in the clay mineral lattice.

TABLE 5

Comparison of the phosphate-replacing ability of different anions

EXTRACTING SOLUTION	PHOSPHORUS REMOVED FROM SAMPLE				TOTAL PHOSPHORUS REMOVED FROM SAMPLE*
	In chloride preleach	In first leachate	In second leachate	During the hour shaking period	
	p.p.m.	p.p.m.	p.p.m.	p.p.m.	p.p.m.
1.0 M NH$_4$Cl	7	8	6	6	20
0.5 M (NH$_4$)$_2$SO$_4$	9	10	8	14	32
1.0 M NH$_4$SCN	9	10	10	10	30
1.0 M NH$_4$C$_2$H$_3$O$_2$	6	17	11	15	43
0.33 M H$_3$BO$_3$ + NH$_4$OH	7	22	12	22	56
0.5 M NaHCO$_3$ + HCl	5	41	30	110	181
0.33 M (NH$_4$)$_2$HC$_6$H$_5$O$_7$	7	75	45	230	350
0.25 M (NH$_4$)$_2$C$_2$O$_4$	7	78	60	467	605
1.0 M NH$_4$F	6	447	162	168	777
H$_2$O	5	15	13	23	51

* Does not include chloride preleach.

From this work with neutral salts it appears that the "replacing" ability of the different anions is in the following order: fluoride > oxalate > citrate > bicarbonate > borate > acetate > thiocyanate > sulfate > chloride. The order given by Russell and Prescott (12) for the ability of soils to adsorb different acids is oxalate > citrate > phosphate > sulfate > chloride > nitrate. Demolon (4) showed that citric acid removed soil phosphate more easily than either acetic or nitric acid of equivalent concentrations.

DISCUSSION

In soils literature, there has been too much quibbling as to whether soil-phosphate reactions should be designated as "adsorption" or "precipitation." In this paper, the term "adsorption" is used in accordance with the definition that adsorption is a difference in concentration of any constituent between the interface and the interior of the neighboring phases (2). This definition does

does not specify the nature of the forces acting, and such a reaction may take place either on the surface of, or in an ion swarm about, the particle. Furthermore, complete reversibility is not implied for many types of adsorption. Application of the term "adsorption" is also justified from the standpoint that there is no apparent stoichiometry involved, and that the amount of phosphate taken up is apparently a function of the concentration present in solution. Furthermore, the phosphate retained by the soil comes into solution more nearly in proportion to the amount present than in a constant concentration characteristic of the solubility of a compound or a series of compounds of low solubility.

Phosphate adsorption does not take place by any single mechanism, and there is no sharp division between the adsorbed phosphate which is immediately available to plants and that which is only slowly available. To illustrate this point, the data in table 3 may be cited to show that the phosphate ions may take part in further reactions after they have been removed from solution. This is evidenced by the decrease in solubility which must be attributed to reorientation of the ions after they had already been adsorbed. From a practical standpoint, the existence of these several forms of phosphate in soils makes it necessary for the soil chemist to recognize at least those forms which are important in his region. Dickman and Bray (6) recognized different phosphate forms when they set up the tentative phosphate fractions which were the basis of the fractionations reported in table 3.

The concept of anion adsorption as a property of soil colloids has been suggested on numerous occasions, but its acceptance has been retarded because no quantitative definition or accepted method of determination has been developed for either adsorbed anions or anion-adsorption capacity.[3] Although adsorbed anions are not necessarily exchangeable, it is probable that this is frequently the case and there is doubtless some advantage in developing an analogy between cation and anion adsorption. In equilibrium studies both with phosphate and with cations, it can be demonstrated that the adsorption may follow Freundlich's equation and this is typical for polar adsorptions of which exchange adsorption is an important type. With base-exchange reactions, other cations are released in amounts equivalent to those adsorbed. The quantitative ion-for-ion exchange which is approximated in replaceable base reactions has not been quantitatively demonstrated for anions, but qualitative evidence of such replacement is abundant (4, 6, 9, 14). Adsorbed cations are readily released by other cations, but there is a definite tendency for some to be held more tightly than others. Furthermore, the slight release by water alone may be thought of as hydrolysis, that is, replacement by the hydrogen ion of water. Similarly, the anions vary as do cations in their replacing ability, but the magnitude of variation among different anions is so great compared to the variation among cations, that

[3] While this paper was being written, both C. S. Piper (Soil and Plant Analysis, Interscience Publishers, New York, 1944) and L. A. Dean and E. J. Rubins (The determination of the exchangeable phosphorus and the anion exchange-absorption capacity of soils, U. S. Dept. Agr. Div. Fert. Invest. Res. Rpt. 40, 1944) have proposed methods for determining replaceable anions and replaceable anion capacity.

the similarity in the two reactions is likely to be overlooked. Hydrolysis, which with anions may be thought of as replacement by the hydroxyl ion of water, is proportionately great, especially when large amounts of adsorbed phosphate are present. Phosphate adsorption in terms of milliequivalents is small and the concentration as well as the replacement by the hydroxyl of water is, therefore, much greater in proportion than with the cations. The pH of the system may be regarded as influencing both cation and anion exchange through its effect on the competition from hydrogen and hydroxyl ions, respectively. For the benefit of the analogy between anion and cation adsorption, it may be pointed out that even "phosphorus fixation" has its counterpart in "potash fixation."

It is frequently argued that soil colloids are negatively charged and cannot exhibit anion adsorption. Since the colloid particle, however, is made up of both positive and negative layers, the over-all negative charge does not preclude the existence of local areas of positive charge where adsorption of negative ions could take place. If a clay were composed entirely of cubical particles of 0.1μ diameter and possessed a base-exchange capacity of 50 m.e., the exchangeable cations would occupy considerably less than 50 per cent of the area of the surface. Of the remaining area only about 2 per cent would be occupied by 100 p.p.m. of phosphorus adsorbed in the form of the phosphate ion. This adsorption might take place either at points where hydroxyl, silicate, or organic anions could be exchanged or at points where aluminum or iron ions were exposed on the surface. If hydroxyl ions are present where iron and aluminum occur at the lattice edge, adsorption at these points would be essentially an exchange of hydroxyl and phosphate ions. In view of the platelike forms of most soil clay particles, the actual surface available for both cation and anion adsorption is much greater than in the cubical particles postulated for the foregoing example.

SUMMARY

This paper reports an investigation of the nature of the reactions responsible for the removal of phosphate ions from solution by soils.

The general procedure in studying phosphate adsorption by soils was to bring samples of the soil into contact with solutions of known phosphate concentrations and to determine the decreases in the amounts of phosphate in solution after definite periods of time. Adsorption curves obtained in this manner with different soils and at different ratios are similar in shape and could be expressed by an equation of the Freundlich type. The forms of the adsorbed phosphate were studied by determining the ease with which the phosphate could be removed by water and other extracting solutions.

Extractions of stored samples of soils to which phosphate had been added 3 years before recovered over 90 per cent of the added phosphate. In these extractions, three fractions; namely, water-soluble, adsorbed (that is, removed by $1 N$ NH_4F), and easily acid-soluble, were determined. These results showed that with additional time there was not only a gradual increase in the amount of phosphate adsorbed but also a gradual change in the status of the adsorbed phosphate. This was shown by decreases in the amounts of phosphate which

could be removed by water in successive extractions and by an increase in the easily acid-soluble fraction. The bulk of the added phosphate, however, was retained in the adsorbed form from which it was displaced by the fluoride ion in a neutral solution.

The phosphate-replacing abilities of several different anions were studied and an analogy between anion and cation adsorption was briefly developed and discussed.

This study aids in understanding how added phosphate is taken up by the soil and held against loss by leaching but still exists in forms which may be utilized by plants. This research gives evidence that so-called "phosphate fixation" is not a serious problem in Illinois soils, and that phosphate fixation, therefore, has no justification as an argument against the use of soluble phosphate fertilizers.

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RELATION BETWEEN POTASH IN SOILS AND THAT EXTRACTED BY PLANTS[1]

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Soil scientists have tried for many years to develop chemical methods for ascertaining the potash requirements of different soils for the production of various crops (1, 2, 3, 4, 5, 7).[3] These efforts have resulted in varying degrees of failure and success. Many of the methods have been tried in Alabama with very little success. It is probable that one of the factors contributing to the failure of chemical tests is the capacity of different soils to supply plants with different amounts of potassium from nonexchangeable forms. Plot experiments have revealed, for example, that Cecil clay has a tremendous capacity to rebuild its supply of exchangeable potash, whereas Hartsells very fine sandy loam has a very low capacity. Small applications of potash maintained yields on the former soil, whereas large applications were needed on the latter; yet the Hartsells soil had twice as much exchangeable potash as the Cecil. Because of these observations, an experiment was undertaken to determine the relation between several forms of potassium in important agricultural soils in Alabama and the amounts of potash extractable from the soils by continuous cropping under greenhouse conditions.

EXPERIMENTAL TECHNIQUE

Ten agricultural soils of Alabama were selected that were known to vary widely in exchangeable potassium, total potassium, exchange capacity, percentage base saturation with respect to potassium, mineralogical composition, and origin (table 2). Twelve 2-gallon pots were filled with thoroughly mixed surface soil of each type. The soils were cropped continuously with a series of agricultural plants until all growth failed because of a deficiency of potassium. Other plant-food elements were supplied as needed.

Only the tops of the crops were harvested. After each crop was grown, the soil in the 12 pots was thoroughly composited and divided equally among the 12 pots before the next crop was planted. The soils were thoroughly leached to remove excess salts after the fourth and eighth crops. The leachates were analyzed for potassium, and the amount leached out was added to the soil as potassium chloride. There was no evidence of toxicity during the experiment.

Determinations were made of the amounts of potassium removed by each crop

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[1] Contribution from the department of agronomy and soils, Alabama Agricultural Experiment Station, Auburn, Alabama. Published with the approval of the director.

[2] Graduate assistant and head of department, respectively. Manuscript prepared by junior author.

[3] Bray, R. H., and DeTurk, E. E. The Illinois potash test. Mimeographed Pamphlet, Agron. Dept., Ill. Agr. Exp. Sta.

and the amounts of exchangeable potassium in the soil at the beginning and end of the experiment. Determinations were also made for total potassium and exchange capacity.

Total potassium in the soil was brought into solution by means of a sodium carbonate fusion; the exchangeable potassium was extracted from the soil with normal ammonium acetate; and the potassium in plant tissue was brought into solution by ashing the tissue and dissolving the ash in acetic acid. In all cases

TABLE 1

Amounts of potash taken from 10 Alabama soils by continuous cropping for 4 years without addition of potash, but with addition of adequate amounts of other plant nutrients

Soil No.	Soil type	POUNDS PER ACRE OF K₂O TAKEN FROM THE SOIL BY DIFFERENT CROPS*													PERCENTAGE OF AVAILABLE K₂O REMOVED		
		Soy-beans 1939	Vetch 1939–40	Peanuts 1940	Cotton 1940	Vetch 1940–41	Peanuts 1941	Sorghum 1941	Winter peas 1941–42	Sorghum 1942	Lupines 1942–43	Peanuts 1943	Sorghum 1943	Total 12 crops	First four crops grown	Second four crops grown	Last four crops grown
3	Tifton sandy loam	28.4	13.0	18.0	8.8	2.6	8.9	4.5	1.9	0.7	0	0.3	0	87	78	21	1
11	Cecil clay loam	15.8	13.8	18.9	7.9	7.3	16.2	5.8	5.1	1.5	0.4	2.1	0.4	95	59	36	5
9	Colbert very fine sandy loam	28.4	13.4	14.7	10.7	5.3	13.6	5.7	2.8	1.1	0	0.6	0	96	70	28	2
1	Orangeburg sandy loam	25.6	4.9	28.4	15.4	2.9	16.2	3.0	8.8	1.9	0	0.5	0	108	69	29	2
13	Savannah very fine sandy loam	33.7	17.0	41.8	12.2	11.2	11.7	4.4	4.7	1.4	0	0.3	0	138	76	23	1
8	Clarksville sandy clay loam	31.5	18.6	33.8	26.8	13.6	1.6	7.4	4.9	2.3	0.5	0.1	0	141	78	20	2
12	Hartsells very fine sandy loam	30.2	21.7	40.7	15.5	7.5	15.8	5.5	3.9	1.3	0	1.0	0	143	76	23	1
7	Durham fine sandy loam	37.7	25.5	36.1	15.3	10.1	26.8	6.5	10.1	1.7	0.1	1.2	0.4	172	67	31	2
10	Decatur clay	22.5	38.2	58.2	24.2	19.7	25.4	8.2	6.1	3.0	0.9	1.3	1.1	209	69	28	3
6	Davidson clay loam	33.0	53.2	61.5	25.1	15.1	36.9	7.0	6.1	2.2	0.6	0.8	0.4	242	71	27	2
	Average..............	28.7	21.9	35.2	16.2	9.5	17.3	5.8	5.4	1.7	0.3	0.8	0.2	143	71	27	2

* Figures represent the average for 12 replicates of each crop on each soil.

the potassium was precipitated as the cobaltinitrite salt and titrated with permanganate according to the method of Volk (6).

RATE OF REMOVAL OF POTASSIUM FROM SOILS BY PLANTS

Plants rapidly extracted the available potassium from the ten soils used. The rate with which the exhaustion of potassium took place is shown in table 1. Very little readily available potassium remained in any of the soils after the eighth consecutive crop was grown, and in some cases yields dropped significantly after the third crop. The last three crops planted failed to live long enough to extract more than a trace of potassium from any of the soils. The peanut plant,

which is a vigorous feeder on potassium as is evidenced by the data presented in table 1, failed completely as the eleventh crop. The soils were allowed to stand 4 months between the harvesting of the eleventh crop and the planting of the twelfth, but the twelfth crop, sorghum, was also a complete failure.

From these results it is apparent that under conditions where year-round cropping is practiced, readily available potassium may be depleted from soils very rapidly. Results of certain cropping systems on the Alabama Substations and Experiment Fields substantiate this conclusion: that is, it has been necessary to increase the rate of potash from 24 pounds per acre to 48 pounds where more than one crop is grown during a 12-month period.

RELATION BETWEEN DIFFERENT FORMS OF POTASSIUM IN SOILS AND TOTAL AMOUNT EXTRACTED BY CONTINUOUS CROPPING

After 12 crops had been grown, chemical analyses of the soils and plant material showed that 39 to 87 per cent of the potassium removed from the soil by the crops came from forms that were nonexchangeable at the start of the test. In all cases the plants removed more potassium than can be accounted for by the drop in exchangeable potassium. This is undoubtedly due to the well-recognized fact that an equilibrium exists in the soil between exchangeable and nonexchangeable forms of potassium. As an average for all of the soils studied, two thirds of the potassium used by the plants existed in the soil in nonexchangeable forms at the beginning of the test (table 2). The fact that such a large and variable amount of nonexchangeable potassium may be utilized by plants probably contributes to the poor relationship found between the amount of exchangeable potassium in soils and the response of plants to applications of potassium. For example, Durham soil that contained only 66 pounds of exchangeable potash per acre supported plant growth until the exchangeable potash was reduced to 29 pounds per acre, and released 172 pounds of potash for plant consumption (table 2). These figures are compared with those obtained for Colbert very fine sandy loam, in which the original soil contained 62 pounds of exchangeable potash per acre, failed to support plant growth at 40 pounds per acre, and released only 96 pounds of potash for plant consumption. Other comparisons of a similar nature show that a simple determination of exchangeable potassium is not a reliable measure of the potassium-supplying power of the soil. Of course, it should be recognized that under field conditions the soil will have a better opportunity to rebuild the supply of exchangeable potassium. In this study the soils were not allowed to rest any appreciable length of time; nevertheless, the amount of nonexchangeable potassium released was very high. Had the same number of crops been grown over a 12-year period (one crop a year), a great deal more nonexchangeable potassium might have been removed and better growth might have been obtained for the last six or eight crops. Since all soils were treated alike in the test, however, the data definitely show that soils differ greatly in their capacity to release potassium from nonexchangeable forms.

Continuous cropping in the greenhouse reduced the exchangeable potassium in all soils to less than 100 pounds of potash per acre, but the percentage drop

was much greater for some than for others. For example, exchangeable potassium dropped about 72 per cent in Davidson soil and only about 23 per cent in Cecil. A study of the data in table 2 reveals the inconsistencies in the relation between the total amount of potassium removed by 12 crops and the amounts of exchangeable potassium in the soil before and after cropping.

Some investigators have shown that the percentage potassium-saturation of the exchange material is a factor in potassium nutrition of plants. The results presented in table 2 indicate that several exceptions to such a relationship exist for the ten soils studied. Durham fine sandy loam, for example, was 2.4 per

TABLE 2

The amounts of several forms of potash in ten Alabama soils, the exchange capacity, and the percentage saturation with potassium

SOIL NO.	SOIL TYPE	POUNDS OF K_2O PER ACRE							PERCENTAGE K SATURATION	
		Total amount extracted by 12 crops	Exchangeable at start of experiment	Exchangeable after 12 crops were grown	Exchangeable form used by 12 crops	Nonexchangeable form used by 12 crops	Total in the soil	Exchange capacity	Before cropping	After cropping
3	Tifton sandy loam	87	52	18	34	53	1,410	1,320	3.9	1.4
11	Cecil clay loam	95	52	40	12	83	6,550	2,250	2.3	1.8
9	Colbert very fine sandy loam	96	62	40	22	74	4,930	2,310	2.7	1.7
1	Orangeburg sandy loam	108	47	21	26	82	1,770	1,570	3.0	1.3
13	Savannah very fine sandy loam	138	86	40	46	92	8,130	1,910	4.5	2.1
8	Clarksville sandy clay loam	141	112	62	50	91	7,900	2,640	4.2	2.3
12	Hartsells very fine sandy loam	143	110	33	77	66	8,440	2,360	4.7	1.4
7	Durham fine sandy loam	172	66	29	37	135	9,310	2,730	2.4	1.1
10	Decatur clay	209	211	84	127	82	14,450	5,690	3.7	1.5
6	Davidson clay loam	242	170	47	123	119	15,250	3,410	5.0	1.4
Average for 10 soils..........		143	97	41	55	88	7,814	2,619	3.6	1.6

cent saturated with potassium, and it released 172 pounds of potash per acre; whereas Clarksville sandy clay loam, which was 4.2 per cent saturated with potassium, released only 141 pounds of potash to the plants. Both soils had about the same total base-exchange capacity (table 2). Several other similar comparisons could be made. Thus there appears to be no definite relationship between the amounts of potassium extractable from soils by continuous cropping in the greenhouse and the amounts of exchangeable or total potassium in the soil, or the percentage potassium-saturation. The capacity of soils to release potassium from the nonexchangeable forms appears to be a dominant factor in the potassium nutrition of plants.

SUMMARY AND CONCLUSIONS

This study was undertaken for the purpose of determining the relation between several forms of potassium in soils and the amounts of potassium extractable from the soils by continuous cropping under greenhouse conditions. Ten soils were exhausted of available potassium by continuous cropping, and determinations were made of the amounts of potassium removed. Determinations were also made of the amounts of exchangeable potassium in the soil before and after cropping, of the total potassium in the soil, the exchange capacity, and the percentage potassium-saturation. From the results of the study the following conclusions may be drawn:

Continuous cropping of 10 Alabama soils with a series of different crops quickly depleted the readily available potassium to the extent that the soils would not support plant growth, even though adequate amounts of plant-food nutrients with the exception of potassium were supplied.

The plants utilized nonexchangeable potassium heavily, yet the amount of nonexchangeable potassium consumed bore no relation to the total potassium extracted by the crops, the total potassium in the soil, or the decrease in exchangeable potassium that resulted from cropping.

An average of two thirds of the potassium used by the plants came from forms that were nonexchangeable at the beginning of the test, and the amount of nonexchangeable potassium removed from the different soils varied between 39 and 87 per cent of the total amount of potassium consumed by the plants.
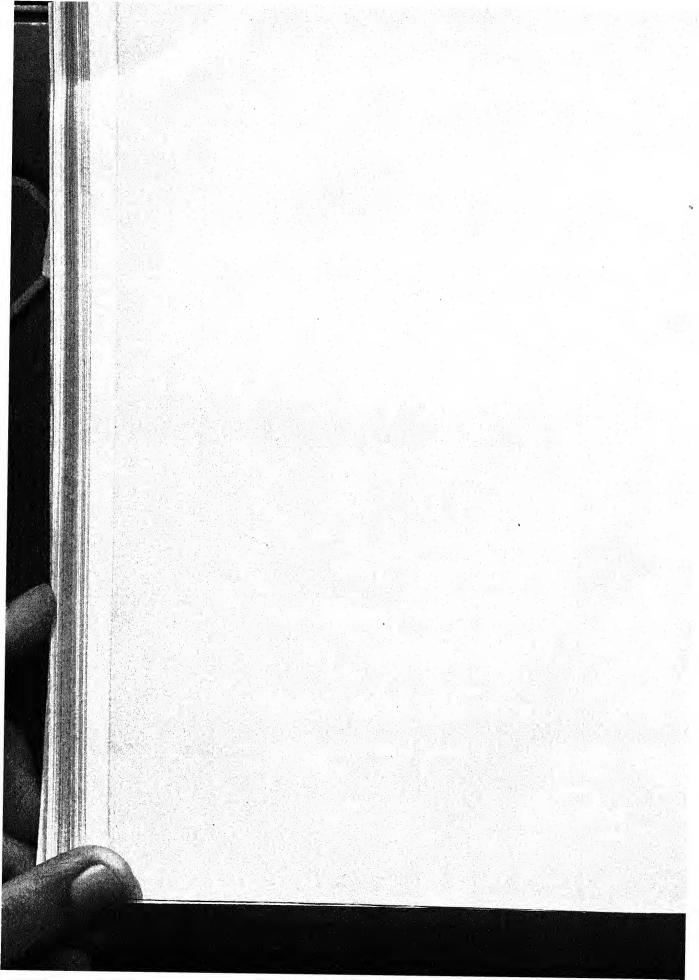
No close relationship was found between the potassium removed by the crops and the exchangeable potassium in the soil, removed from the soil, or remaining in the soil after cropping. Trends were evident.

Neither the exchange capacity of the soil nor the percentage potassium-saturation showed a definite relationship to the amount of potassium extracted by the plants.

The variability of the capacity of different soils to release potassium from the nonexchangeable forms for plant consumption appears to be a dominant factor in the nutrition of plants, and the magnitude of this factor is difficult to measure through the use of chemical soil tests.

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COMPARISON OF FOUR METHODS OF SOIL MOISTURE MEASUREMENT

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Quantitative information on soil moisture is an essential part of many agronomic, hydrologic, and other related investigations. It has practical applications in determining irrigation requirements and moisture reserves.

The need for quantitative information on soil moisture has led to the development of a number of methods for its measurement. Various principles have been employed. These include electrical resistance (4, 5, 7, 8, 21), capacitance (3, 10), thermal conductivity (17, 18), film tension (13, 16), mechanical resistance (1), and the gravimetric determination of water sorbed by porous mediums (6, 14). The theoretical considerations involved have been reviewed by Edlefsen and Smith (9).

All of the methods appear to have some limitations in use, and few, if any, have been tested adequately with respect to their relative applicability to general conditions of soil moisture measurement. In any single investigation the number of measurements made and the variety of soils available are necessarily limited.

In the present study an attempt has been made to obtain comparable data on the accuracy and general suitability of four different methods of measurement. The direct determination of soil moisture on oven-dried random samples is included to furnish basic data on soil moisture variability. The tensiometer (13) is included on the assumption that it gives as direct a measure of moisture potentials as random sampling does of moisture percentages. Two methods for the indirect determination of moisture percentages or potentials are also included. These are the resistance block method of Bouyoucos and Mick (4) and the gravimetric plug[2] method of Davis and Slater (6). The design of the Slater-Davis instrument that was used in these tests differs from that originally described in that air vents, plug interior of sand, and a rod to displace air from the well tube are eliminatd from the design. The complete unit, as it was used in this investigation, is shown in figure 1.

On the basis of available information each method of moisture measurement that was selected appeared to represent the most practical application of some one principle of measurement. Methods employing other principles were

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[2] Richards and Weaver (14) apply the term "sorption block" to a moisture-measuring instrument that is similar in principle. The term is avoided in this paper, since both the gravimetric plug and the resistance block are sorption devices.

eliminated in preliminary studies as insufficiently developed for field testing or as useful only under restricted conditions.
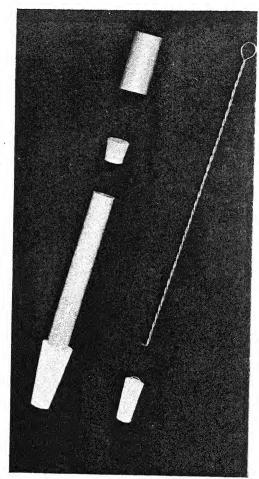
FIG. 1. GRAVIMETRIC PLUG ASSEMBLY

Left: Gypsum casing and attached synthane tube which are placed vertically in the soil, with stopper and cap. The tube is 1 inch in diameter. Right: gypsum plug with corrosion-resistant wire loop in upper end, and hooked wire for manipulating plug.

DESIGN OF THE EXPERIMENT

An area of Beltsville silt loam 40 feet square was selected for uniformity and laid off in four square blocks. These were again subdivided into plots 10 feet square. A moisture instrument was installed at the center of each plot. The instruments were tested in triplicate, so that actually only three of the four blocks are represented in the tests.

In order to evaluate instrument results, moisture determinations were made on soil samples that were taken from each plot. A grid system was used to locate

the samples at random in an area approximately 6 feet in diameter surrounding each instrument. An area approximately 1 foot in diameter around each instrument was omitted from the random sampling to avoid any disturbance of the instrument. Soil samples were taken in duplicate from each plot about 20 times each season. The samples were representative of a 4-inch intercept at the moisture instrument level and were taken with a King tube.

Instruments were read on a daily schedule. Rainfall and temperature records were kept.

In 1941 and 1942 the test area was kept under a cover of clipped bluegrass. In 1943 the blocks were spaded, and four surface conditions were imposed. The conditions were bare uncultivated soil, bare soil cultivated about 1 inch deep after each rain, a straw mulch about 1 inch deep and equivalent to 10 tons per acre, a cover of Italian rye grass.

A second test area was laid out in 1943 on Muirkirk sand in an identical design except that the bare uncultivated plots were omitted to relieve somewhat the burden of sampling. On this loose soil it appeared that shallow cultivation made no appreciable modifications of surface conditions, and little was to be gained by maintaining both types of bare plots.

Data on soil moisture and its measurement were collected in all three seasons, 1941–1943.

Data obtained in 1941 were preliminary in character, particularly with respect to the gravimetric plugs,[3] and were a near failure with respect to tensiometers, due to drought conditions that kept moisture levels below the effective range of the instrument.[4]

In 1941 and 1942 moisture instruments were tested at two depths, 6 and 18 inches. Instrument response at 18 inches showed no phenomena that were not characteristic of the same type of instrument at the 6-inch depth, and was limited by a reduction in moisture fluctuations.

In 1943 instruments were installed at the 6-inch depth only. Drought conditions again vitiated many of the tensiometer readings.

The operation of the resistance blocks and the gravimetric plugs can be judged by their 1942–43 data at the 6-inch depth. In the interests of brevity, these data and the corresponding 1942 data for tensiometers have been selected for consideration.

PRESENTATION OF DATA

Comparison of responses of single instruments to rainfall

A record of rainfall, and some results that were obtained from single instruments during the 1942 season are shown in figure 2. The graphs indicate (and allow some comparison of) the types of data that are characteristic of the in-

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[3] The data have been reported in part (6).

[4] Out of a total of 1,078 instrument days on which observations were made, 788 days or 73 per cent were characterized by tensions greater than 60 cm., the generally accepted limit of tensiometer operation (12).

struments. They serve also to introduce the units of measurement in which instrument response to moisture has been recorded. Tensiometers have been
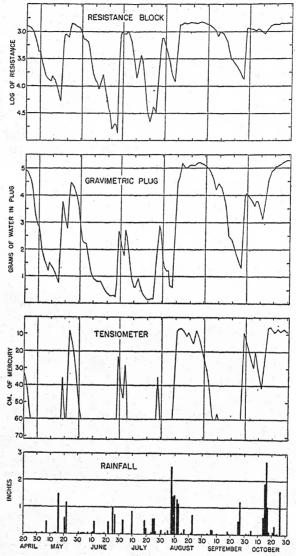
FIG. 2. RESPONSES OF RESISTANCE BLOCK, GRAVIMETRIC PLUG, AND TENSIOMETER
TO RAINFALL

Time series of readings from one instrument of each kind, in silt loam soil at a 6-inch depth, 1942 season.

read directly in centimeters of mercury. Plug readings are given in grams of water sorbed by the plugs. The logarithms of ohms resistance rather than readings in ohms are adopted for recording the responses of the resistance blocks

to facilitate the application of temperature corrections.[5]   Also, it will be seen later that the use of logarithms gives a linear relation between resistance block readings and soil moisture and so makes the block data more readily comparable to the corresponding plug and tensiometer data.

The curve for tensiometers in figure 2 has been limited arbitrarily to tensions of 60 cm. or less.   A continuous curve for tensiometers cannot be shown because of the failure of these instruments at the lower moisture levels.   Both the resistance blocks and the gravimetric plugs are capable of furnishing an unbroken sequence of readings.

Response of all the instruments to rainfall is prompt, as is shown by the manner in which each of the curves ascends abruptly following each increment of effective rainfall.   Sequences of daily readings delineate the descending segments of the curves, and their smoothness indicates a marked consistency in the day-to-day behavior of each of the instruments.

The major changes in moisture levels are duly recorded by each instrument. Peaks are sharpest in the tensiometer curve and indicate that this instrument is the most sensitive at the higher moisture levels.   The effect is most marked during August and October when the heaviest rainfall occurred.

A broadening of the peaks is most characteristic of the resistance blocks.   The gravimetric plug holds an intermediate position with respect to sensitivity in the wettest conditions that were encountered.

The blocks and plugs may be compared in their response to the driest conditions that occurred in June and July.   Small rains occurred then that caused slight changes in the gravimetric plugs.   A somewhat greater effect was evident in the resistance blocks.   The comparisons indicate that the sensitive range of the blocks is slightly lower than that of the plugs in terms of moisture levels.

Field behavior of tensiometers

The response of tensiometers to soil moisture as determined by random sampling is shown in figure 3.   The graph includes data from three instruments in different plots.   Both instrument variability and the variability of soil moisture may be effective in causing some dispersion of the data.   It is evident, however, that an approximately linear relationship exists for the data at tensions of less than 60 cm., and that at tensions greater than 60 cm. little or no correlation is evident between soil moisture and instrument readings.

Whether any of the variance that is indicated by figure 3 for tensions of less than 60 cm. is due to differences in response among the three instruments is indicated by the analysis of variance given in table 1.   The sum of the devia-

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[5] Temperature corrections were made on the resistance block readings according to the equation

$$\text{Log } R_{(t-70)} = \text{Log } R_t [1 + 0.002 (t - 70)]$$

where R is the resistance in ohms and t is the temperature in degrees Farenheit.   The equation is an essential agreement with the temperature correction curves of Bouyoucos and Mick (4).   (By personal communication from T. C. Peele.)

tions squared for a single trend line amounts to 74.2606. By calculating a separate regression coefficient for each instrument, the sum of the deviations squared is reduced to 72.3713. The small difference of 1.8893 is not significant.

A similar test for uniformity of instrument response will be made later in the case of the resistance blocks and gravimetric plugs on the more extensive data that are available for testing these instruments. However, their 1942 data[6]
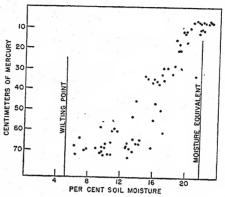
FIG. 3. RELATION OF TENSIOMETER READINGS TO SOIL MOISTURE
OF BELTSVILLE SILT LOAM

Three Instruments, bluegrass cover, 1942

TABLE 1

Test of regressions for estimating soil moisture from instrument readings (days within plots), Beltsville silt loam, 1942

REGRESSIONS USED	SOIL MOISTURE ADJUSTED FOR REGRESSION WITH INSTRUMENT READINGS								
	Gravimetric plugs			Resistance blocks			Tensiometers		
	Df	Sum of squares	Mean square	Df	Sum of squares	Mean square	Df	Sum of squares	Mean square
Single regression within plots	44	26.6327	0.6053	26	43.4485	1.6711	38	74.2606	1.9542
Separate regressions for three individual plots..........	42	25.8612	0.6157	24	38.8747	1.6198	36	72.3713	2.0103
Difference for testing separate regressions..........	2	0.7715	0.3858	2	4.5738	2.2869	2	1.8893	0.9446

only are considered in table 1 for a direct comparison with tensiometer behavior. The reductions in sums of squares for these instruments through the use of separate regressions for individual plots are likewise nonsignificant.

The significance tests of table 1 show that a single error of estimate is adequate to characterize the relative accuracy of each type of instrument as far as that can be judged by the 1942 data. Errors of estimate are reported in table 2. The highest error recorded, 1.40 per cent, is associated with tensiometers. This

[6] The data are restricted to the moisture ranges in which the instruments are sensitive.

error is notably higher than the corresponding standard deviation of duplicate soil moisture samples of 0.66 per cent, a value which marks the probable limit of accuracy that could have been expected from perfect instrument operation. In contrast, the gravimetric plugs had an error of estimate of 0.78 per cent, a value that is essentially identical with the corresponding error of random soil-moisture sampling.

The regression of soil moisture (x) on tensiometer readings (y) is given by the equation $x = 22.22 - 0.132y$. Based on this equation, the range covered by the instrument between tensions of 0 and 60 cm. extends from 22.22 per cent to 14.30 per cent of soil moisture, an absolute range of 7.92 per cent. Since the error of estimate is 1.4 per cent, the range of effective operation for tensiometers is about 5.7 times the error of estimate.[7]

Investigations of tensiometric devices for measuring soil moisture have been made over a period of more than 30 years (10) and have included a number of studies of their use under field conditions (5, 11, 14, 15). The consensus of these

TABLE 2

Standard errors of estimating soil moisture by three kinds of instruments in comparison with the corresponding standard deviations of soil moisture determinations, Beltsville silt loam, 1942

TYPE OF INSTRUMENT	STANDARD ERROR OF ESTIMATING SOIL MOISTURE BY INSTRUMENT*	STANDARD DEVIATION BETWEEN DUPLICATE SOIL MOISTURE SAMPLES
	per cent	*per cent*
Tensiometers..................................	1.40	0.66
Resistance blocks............................	1.29	0.83
Gravimetric plugs...........................	0.78	0.80

* Based on the respective moisture range in which each instrument is sensitive.

studies is that tensiometers respond satisfactorily to soil moistures at tensions not greater than 60 cm., but varying opinions are current about their general suitability for field use. The practical value of an instrument for field measurements depends on a number of factors other than the accuracy of its response.

In the present investigation tensiometers did not appear to be adapted generally to field use. Their near-failure in two years out of three due to drought conditions has already been noted and emphasizes the inadequacy of their range for conditions often encountered in the field. Even in 1942, a season of abundant and well-distributed rainfall, the soil-moisture content under grass was often too low to be recorded by the tensiometers. This was illustrated in the time series curve of figure 2, and was evident from another point of view in figure 3

[7] The ratio of the range of an instrument to its error of estimate has been termed its *efficiency of differentiation* and is used elsewhere in this paper to characterize the relative performance of plugs and blocks as well as tensiometers. The ratio is a better measure of the utility of an instrument generally than is the error of estimate alone, since the degree of differentiation in soil moisture of which an instrument is capable within its range depends on both the length of the range and the error of estimate.

where tensiometer readings were plotted against corresponding soil-moisture determinations.

Tensiometers were kept in operation with little effort during moist periods. In dry weather, however, daily care was required to keep the instruments in working order. Even though the water columns did not always break, air accumulated in the traps in some quantity. This resulted in a response on the part of the instrument to both air and soil temperature changes, and made impossible any consistent correction for temperature effects.

On a number of occasions, leaks developed in the tensiometer systems. In the several cases where an unmistakable break occurred, no particular difficulty was encountered except for the labor required to locate and repair the break. Leaks of lesser magnitude were more common and far more serious, since they could remain undetected and, by undue irrigation of the soil in the vicinity of the porous cup, cause a lowering of the daily readings. It was often difficult to judge whether the loss of water from the tensiometers at tensions between 40 and 65 cm. was "normal" or whether some adventitious leakage was taking place. In the present investigation the operators were aided by repeated checking against other instruments and the actual soil moisture determinations. Under the usual conditions of field operation the operator must accept the reading of the tensiometer as correct or exercise personal judgment in the elimination of questionable data.

It is the experience of the writers that tensiometers are subject to mechanical failure. Their cost prohibits extensive replication, and there is no way, once a tensiometer is installed under field conditions, of determining easily whether or not it is functioning correctly.

Water-filled tensiometers, such as were used in this investigation, cannot be operated in freezing weather.

Comparison of field behavior of resistance blocks and gravimetric plugs

Comparisons based on daily changes in soil moisture. The response of resistance blocks to soil moisture as determined by random sampling of the Beltsville silt loam soil is shown in figure 4. Their response in Muirkirk sand is shown in figure 5. The corresponding data for gravimetric plugs are given in figures 6 and 7.

An inspection of these figures indicates that both instruments have some limitations with respect to the measurement of soil moisture. An essentially linear regression of instrument readings on soil moisture is evident generally in the intermediate moisture ranges, but in the highest levels of moisture encountered the wide horizontal dispersion of the data on the graphs shows that both instruments fail to respond satisfactorily to soil moisture changes. Some insensitivity is to be noticed with the gravimetric plugs among the lowest values of soil moisture encountered.

It seemed evident from this plotting that any further analysis of the data should be limited to the range in which each of the instruments showed an appreciable response to soil moisture changes. This procedure had been followed

with the tensiometers.   The selection of range admittedly required an exercise
of personal judgment.
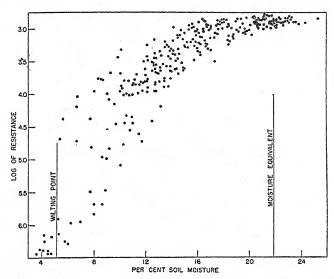
FIG. 4. RELATION OF RESISTANCE BLOCK READINGS TO SOIL MOISTURE OF BELTSVILLE
SILT LOAM

Fifteen instruments, five conditions or covers, 1942–43
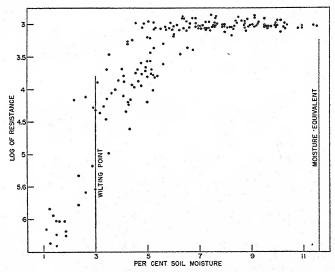
FIG. 5. RELATION OF RESISTANCE BLOCK READINGS TO SOIL MOISTURE OF MUIRKIRK SAND

Nine instruments, three conditions or covers, 1943

Inspection of the graphs showed that the limits of effective operation could
not be fixed in terms of soil moisture percentages if the same limits were to apply
to both soils.   This was to be expected, since the responses of the instruments

are due to changes in pF rather than to absolute levels in soil moisture percentages (9). Limits for each instrument, however, could be selected on the basis of instrument readings that were common to both soils. The range indicated by the data for the gravimetric plugs is 0.10 to 4.59 gm. of absorbed mois-
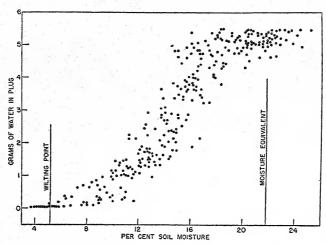
FIG. 6. RELATION OF GRAVIMETRIC PLUG READINGS TO SOIL MOISTURE OF BELTSVILLE
SILT LOAM

Fifteen instruments, five conditions or covers, 1942–43
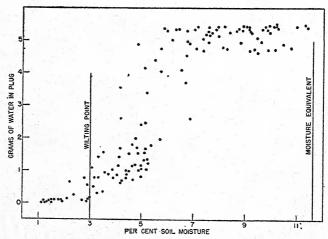
FIG. 7. RELATION OF GRAVIMETRIC PLUG READINGS TO SOIL MOISTURE OF MUIRKIRK SAND

Nine instruments, three conditions or covers, 1943

ture, and for resistance blocks, a logarithm of resistance equal to 3.15 or greater.

Figures 4 to 7 show a considerable dispersion of moisture-instrument data between these limits. Some of the sources of variability are isolated and the instruments are compared as to how well they respond to soil-moisture variation within their ranges of sensitivity in the analyses that follow.

Aside from the fact that instruments of the same type may not be essentially identical in their response to soil moisture, variability in instrument response may (and does) arise from differences in soils, crops, and sequences of moisture conditions. The degree to which separate regressions were necessary for each instrument or condition of test in order to obtain the best estimate of soil moisture is shown in table 3.

Lines A to D of table 3 indicate the variation between direct determinations of soil moisture and determinations by means of instruments when (A) a single

TABLE 3

Tests of regressions for estimating soil moisture from instrument readings (days within plots)

| | SOIL MOISTURE ADJUSTED FOR REGRESSIONS WITH INSTRUMENT READINGS | | | | | |
| REGRESSIONS USED | Gravimetric plugs | | | Resistance blocks | | |
	Degrees of freedom	Sum of squares	Mean square	Degrees of freedom	Sum of squares	Mean square
(A) Single regression for all conditions...................	191	233.0498	1.2202	194	307.0647	1.5828
(B) Separate regressions for two soils.....................	190	155.9569	0.8208	193	184.4366	0.9556
(C) Separate regressions for two soils and 2 years..........	189	140.1384	0.7415	192	179.4565	0.9347
(D) Separate regressions for 24 individual plots.............	168	112.7437	0.6711	171	167.8359	0.9815
Differences for testing separate regressions						
(a) For two soils (A − B)......	1	77.0929	77.0929**†	1	122.6281	122.6281**†
(b) For two soils and 2 years (B − C).....................	1	15.8185	15.8185**‡	1	4.9801	4.9801*‡
(c) For 24 individual plots (C − D)....................	21	27.3947	1.3045*§	21	11.6206	0.5534§

* Significant at 5 per cent level.
** Significant at 1 per cent level.
† Significance tested in comparison with mean squares of line B.
‡ Significance tested in comparison with mean square of line C.
§ Significance tested in comparison with mean square of line D.

regression is used for all conditions, (B) separate regressions are used for the two soils, (C) separate regressions are used for the 1942 and 1943 observations on the Beltsville soil in addition to one regression for 1943 on the Muirkirk soil, and (D) when separate regressions were used for each of the 24 individual plots.

It will be noted that as more regressions are used the sums of squares become smaller. This merely signifies that the variations in estimating soil moisture are progressively smaller the more closely every plot is calibrated for its specific instrument, its cover, or individual soil characteristics. There are obvious advantages, however, in adapting a single regression of blocks or plugs to all

conditions of use, provided the requirements of accuracy can be met. In the case of the plugs, the mean squares are progressively smaller as the number of regressions are increased, and this improvement in accuracy is shown to be statistically significant in the lower part of the table. In the case of the blocks, improvement in accuracy ceased with separate regressions for soils and years.

The standard errors of estimate that correspond to the regressions of table 3 are given in table 4. The standard errors indicate the limit of variation that is to be expected between the estimated and the actual soil moisture in two out of three estimates, and it is therefore evident that, in general, soil moisture can be estimated more closely by plug readings than by block readings

The highest errors of estimate are logically associated with the use of a single regression for all conditions. When separate regressions are used for each soil there is a marked reduction in error, and some further reduction in error is obtainable with the gravimetric plugs in the direction of individual calibrations. The use of individual regressions scarcely seems justified, however, in view of

TABLE 4

Standard errors of estimating soil moisture by gravimetric plugs and resistance blocks, based on different regressions (days within plots)

REGRESSIONS USED	STANDARD ERROR OF ESTIMATING SOIL MOISTURE BY INSTRUMENT*	
	Gravimetric plugs	Resistance blocks
	per cent	*per cent*
Single regression for all conditions............	1.10	1.26
Separate regressions for each soil.............	0.91	0.98
Separate regressions for each soil and year....	0.86	0.97
Separate regressions for each plot............	0.82	0.99

* Based on the respective moisture range in which each instrument is sensitive.

the limited improvement in accuracy that is obtained. It is felt that most users of moisture instruments will be satisfied with separate regressions for each soil, or at most, separate regressions for each soil and year. The choice is a matter for practical judgment.

Table 5 shows the standard errors of estimate that were obtained when these were calculated separately by soils and years for both the blocks and the plugs. It is evident from this table that the accuracy with which soil moisture was estimated by the instrument was not constant but varied according to the conditions of the test. For the plugs, the standard error of estimating soil moisture was 0.94 per cent on Beltsville silt loam in 1943 and 0.76 per cent on Muirkirk sand in the same year. There were even greater deviations, of from 1.29 to 0.56 in the errors of estimate, for the blocks.

The errors of estimate are a result not only of the limitations of the instruments tested, but also of the accuracy with which soil moisture can be estimated by direct determinations. The latter factor is indicated in table 5 by the standard deviation between duplicate moisture determinations that were made directly

on soil samples taken at random on the grid surrounding each instrument. These are seen to be lower on the sand than on the silt loam.

The standard deviation of moisture sampling is generally less than the standard error of estimating soil moisture by means of the instruments, or, direct moisture determinations still appear to be a slightly more accurate method of moisture measurement. The average difference between the direct and instrument methods has been found to be significant in the case of plugs, and highly significant in the case of the resistance blocks.

Comparisons based on seasonal moisture levels. The discussion of resistance blocks and gravimetric plugs to this point has been concerned with the regressions and errors for estimating soil moisture changes from day to day within a plot. Attention can now be given to the reliance to be placed on separate instruments for recording the correct level of moisture on different plots. This

TABLE 5

Standard error of estimating soil moisture by means of gravimetric plugs and resistance blocks, in comparison with the corresponding standard deviations of soil moisture determinations (days within plots)

INSTRUMENT AND CONDITIONS OF TEST	NUMBER OF INDIVIDUAL OBSERVATIONS	STANDARD ERROR OF ESTIMATING SOIL MOISTURE BY MEANS OF INSTRUMENT*	STANDARD DEVIATION BETWEEN DUPLICATE SOIL MOISTURE DETERMINATIONS
		per cent	*per cent*
Gravimetric plugs			
Beltsville silt loam, 1942	48	0.78	0.80
Beltsville silt loam, 1943	114	0.94	0.71
Muirkirk sand, 1943	54	0.76	0.56
Resistance blocks			
Beltsville silt loam, 1942	30	1.29	0.83
Beltsville silt loam, 1943	120	1.05	0.71
Muirkirk sand, 1943	69	0.56	0.50

* Based on the respective moisture range in which each instrument is sensitive.

is shown in tables 6, 7, and 8 by the divergences from average moisture levels that were recorded by different instruments.

Table 6 gives the data for plugs, and table 7, the data for blocks. The instrument data are based on three regressions for each type of instrument: one for the 1942 determinations, a second for the 1943 determinations on Beltsville silt loam, and a third for the 1943 determination on Muirkirk sand.

The differences in moisture level estimates between the instruments and direct soil sampling for each plot were tested for significance by means of the standard *T* test. The difference required for significance varied among the plots because of differences in the number of observations on which the plot averages were based.

The highest significant difference that was recorded for the plugs was −1.25 per cent and for the blocks 1.36 per cent. These differences are significantly

TABLE 6

Differences in mean soil moistures as determined by gravimetric plugs and by soil sampling, within the sensitive range of the instrument

Sampling values are the averages of duplicate determinations

COVER	NUMBER OF OBSER- VATIONS	REPLICATE A Method Sampling	Plug	Difference	REPLICATE B Method Sampling	Plug	Difference	REPLICATE C Method Sampling	Plug	Difference	REPLICATE AVERAGE Number of Obser- vations	Method Sampling	Plug	Difference
		pct.	pct.	pct.	pct.	pct.	pct.	pct.	oct.	pct.		pct.	pct.	pct.
Beltsville silt loam, 1942														
Bluegrass	16	11.08	11.71	0.63**	12.12	11.54	-0.58*	11.80	11.76	-0.04	48	11.67	11.67	0.00
Beltsville silt loam, 1943														
Rye grass	9	10.97	11.74	0.77*	11.58	11.28	-0.30	12.33	11.08	-1.25**	27	11.62	11.37	-0.25
Bare uncultivated	16	12.78	13.21	0.43	14.21	13.97	-0.24	13.86	13.18	-0.68*	48	13.62	13.46	-0.16
Bare cultivated	11	13.53	14.64	1.11**	14.19	13.98	-0.21	14.92	14.80	-0.12	33	14.21	14.47	0.26
Straw mulch	2	10.94	11.70	0.76	12.58	14.80	2.22	11.61	11.67	0.06	6	11.71	12.72	1.01*
Average	38	12.47	13.20	0.73**	13.50	13.38	-0.12	13.69	13.07	-0.62**	114	13.22	13.22	0.00
Muirkirk sand, 1943														
Rye grass	8	5.54	4.98	-0.56	4.45	4.37	-0.08	5.03	4.63	-0.40	24	5.01	4.66	-0.35*
Bare cultivated	5	3.35	4.55	1.20*	4.44	4.45	0.01	4.70	4.52	-0.18	15	4.16	4.50	0.34
Straw mulch	5	4.81	4.68	-0.13	4.02	4.18	0.16	3.67	4.29	0.62	15	4.17	4.39	0.22
Average	18	4.73	4.78	0.05	4.33	4.34	0.01	4.56	4.50	-0.06	54	4.54	4.54	0.00

* Significant difference between two methods of determination at 5 per cent level.
** Significant difference between two methods of determination at 1 per cent level.

TABLE 7

Differences in mean soil moistures as determined by resistance blocks and by soil sampling within the sensitive range of the instrument

Sampling values are the averages of duplicate determinations

COVER	NUMBER OF OBSERVATIONS	REPLICATE A			REPLICATE B			REPLICATE C			Number of observations	REPLICATE AVERAGE		
		Method		Difference	Method		Difference	Method		Difference		Method		Difference
		Sampling	Block		Sampling	Block		Sampling	Block			Sampling	Block	
		pct.	pct.	pct.	pct.	pct.	pct.	pct.	pct.	pct.		pct.	pct.	pct.
Beltsville silt loam, 1942														
Bluegrass.............	10	9.31	10.52	1.21*	9.53	9.18	−0.35	10.75	9.88	−0.87	30	9.86	9.86	0.00
Beltsville silt loam, 1943														
Rye grass.............	16	8.61	8.73	0.12	8.97	8.36	−0.61*	9.50	8.44	−1.06**	48	9.03	8.51	−0.52
Bare uncultivated.....	13	12.09	13.10	1.01**	13.62	13.20	−0.42	13.13	13.61	0.48	39	12.94	13.31	0.37*
Bare cultivated.......	8	12.96	13.35	0.39	13.66	13.44	−0.22	14.06	14.03	−0.03	24	13.56	13.61	0.05
Straw mulch..........	3	11.52	13.43	1.91	13.22	13.84	0.62	12.03	12.80	0.77	9	12.26	13.36	1.10
Average.............	40	10.83	11.43	0.60**	11.74	11.36	−0.38*	11.78	11.57	−0.21	120	11.45	11.45	0.00
Muirkirk sand, 1943														
Rye grass.............	13	3.89	3.43	−0.46*	3.16	3.15	−0.01	3.43	3.10	−0.33	39	3.49	3.21	−0.28**
Bare cultivated.......	5	3.35	4.71	1.36**	4.44	4.68	0.24	4.70	4.46	−0.24	15	4.16	4.62	0.46**
Straw mulch..........	5	4.81	4.69	−0.12	4.02	4.24	0.22	3.67	4.29	0.62	15	4.17	4.41	0.24
Average.............	23	3.97	3.98	0.01	3.63	3.72	0.09	3.76	3.66	−0.10	69	3.79	3.79	0.00

* Significant difference between two methods of determination at 5 per cent level.
** Significant difference between two methods of determination at 1 per cent level.

greater than the errors of estimate that correspond to the regressions on which the instrument data of tables 6 and 7 are based (table 5). These results indicate that the soil moisture estimates obtained from some of the instruments were consistently too high or too low.

The failure of some of the instruments to indicate the correct moisture level was subjected to further examination by means of the analysis of variance in table 8. For the gravimetric plugs, the analysis shows that the discrepancy of the instruments applied to all the variable conditions set up in the experiment, that is, to replicates, covers, and interaction. Thus the plug method estimates (table 6) averaged 0.73 per cent too high for replicate A and 0.62 per cent too low for replicate C. Both values are significant. Plugs set under straw mulch gave estimates 1.01 per cent too high. These divergences for the covers were not consistent, however, in the different replicates, as shown by the significant interaction of table 8.

TABLE 8

Tests of significance of differences between determinations, by moisture instruments and random sampling, of mean soil moistures for replicates and covers

SOURCE OF VARIATION	GRAVIMETRIC PLUGS			RESISTANCE BLOCKS		
	Degrees of freedom	Sum of squares	Mean square	Degrees of freedom	Sum of squares	Mean square
(A) Between plots						
Replicates................	6	46.8662	7.8110**	6	45.6375	7.6063**
Covers....................	5	16.8619	3.3724**	5	35.9158	7.1832**
Interaction replicates and covers.................	10	19.2344	1.9234**	10	14.1949	1.4195
(B) Between days within plots...	189	140.1384	0.7415	192	179.4565	0.9347
Total..................	210	223.1009		213	275.2047	

** Significant at 1 per cent level.

For the resistance blocks, the divergences between the estimated and actual soil moisture levels were likewise significant for some of the covers and replicates (table 8). Examination of the data of table 7 shows that these divergences for the covers were markedly inconsistent in the different replicates, although on the average the inconsistencies, expressed as interaction in table 8, cannot be judged as significant.

A summary can be made now of the factors that have affected the operation of resistance blocks and gravimetric plugs during the course of these experiments. The factors correspond to differences in soils, covers, years, and replications. It has not been possible to isolate the specific causes of variability that are included under these headings. The study shows, however, that there were two general types of variability.

First, differences in soils, sites, and covers induced differences in instrument responses. This was shown by the finding that different regressions were re-

quired for calibrating instruments of the same kind on different soils and was indicated by the divergences between instrument estimates and actual soil moisture for covers and replicates. The induced differences in instrument response on a single soil may be caused by changes in soil structure that are due to management and that modify the basic pF-moisture relationships, and by hysteresis in both instruments and soils.

The second type of variability is caused by differences among the individual instruments themselves. The plot averages of tables 6 and 7 showed that the failures of the installations to give correct estimates could not be entirely accounted for by the influences of the covers and the replicates. In this respect, it should be noted that each instrument installation reflected the moisture conditions at a fixed position, whereas the soil moisture determinations with which the instrument estimates were compared were made on 6-foot grids surrounding the installations. Discrepancies between the estimates by means of instruments and the actual soil moisture determinations therefore could be attributable either to variations among the instruments or to actual differences in soil moisture levels between positions in which the instruments were installed and the places where the corresponding soil samples were taken on the grid. Evidence on this was obtained from the 1943 tests where two instruments (one a gravimetric plug and the other a resistance block) were installed in close proximity at the center of each plot. An analysis of variance showed that the differences in estimated moisture levels between the pairs of instruments were of about the same magnitude as the differences between the average of the instrument estimates and the corresponding direct moisture values. This result indicated that the failure of an installation to give a correct estimate of the soil moisture level when the effects of cover and replications were accounted for was not due in any marked degree to variations in moisture distribution on the plot, but was due chiefly to individual instrument characteristics. It appears, therefore, that reliance can be placed on an instrument to indicate a correct moisture level only if it is first individually calibrated.

Other factors that affect instrument operation. The data that have been presented on resistance blocks and gravimetric plugs show the major similarities and differences that marked their operational behavior, and aside from any advantages or disadvantages that are evident from the analysis, the resistance blocks appear to be adapted to field use in a number of respects:

The units are not difficult to install, and measurements can be made quickly.
The cost of the individual unit is low, and considerable replication is feasible.

Resistance blocks have some disadvantages:

Attention has been directed previously to their insensitivity at the higher moisture levels.
They may be affected materially by electrolyte concentrations; however, no tests of the effects of electrolytes were made in this investigation.
They are affected by temperature. The use of devices to determine soil temperatures, and the subsequent correction of the resistance data, add to the complications of moisture measurement and are in themselves possible sources of error.

Moisture causes a slow disintegration of the resistance blocks due to the semisoluble gypsum of which they are made. In no case did the field conditions of soil and moisture that were encountered from April to November cause any marked change in the appearance of the blocks or in the readings they gave. Relative resistances, however, tended to increase slightly during the season, and blocks left in the ground over winter disintegrated appreciably. This was particularly true where conditions were favorable to heavy leaching. New blocks were installed each year to obtain the data that have been reported.[8]

Like the resistance blocks, the gravimetric plugs that were used in this investigation were subject to disintegration. They were cast from a semisoluble material (hydrocal) as a matter of expediency.

The effects of solubility are confined largely to the casing which protects the plus against disintegration. The dry weight of a plug is about 18 gm. The change in dry weight from April to November has never exceeded ± 0.05 gm.

In other respects the present unit appears to be of a practical design. The units are easily installed and may be produced at low cost. Readings can be made quickly, although not so quickly as on resistance blocks. In many cases a balance for weighing the plugs will be available without purchase. Plugs can be weighed at the instrument location or placed in small closed containers and weighed at some central point.

The gravimetric units are not materially affected by temperature or electrolyte concentrations, and no corrections of the basic data are necessary. The instrument responds to temperature only as temperature potentials cause a translocation of soil moisture.

Some protection against trampling is needed at field locations, and under some conditions the units are subject to heaving by frost action.

Gravimetric units have not been produced commercially. The tests that have been made of their behavior are considered to be tests of a principle of measurement rather than tests of a perfected instrument.

Comparison of utility of plugs, blocks, and tensiometers. The lack of complete data on tensiometers has prevented any step-by-step comparison of this instrument with plugs and blocks. The 1942 data only of the plugs and blocks were introduced into the discussion of tensiometers to compare the errors of estimate of the three instruments in that one year. It is desirable now to make comparisons among the three instruments on the basis of the total data that are available; and to summarize their field behaviors with respect to their errors of estimate, the proportion of the available moisture range they cover, and their

[8] Slater (19) describes a cylindrical resistance block, cast from hydrocal, with an electrode shield that eliminates current flow outside the confines of the block itself. Blocks of this type have been in continuous use for 3 years in silt loam soil under local conditions, and upon removal were found to be in fair condition. Bouyoucos and Mick blocks (purchased and presumably cast from plaster of paris) were removed at the end of 2 years in bad condition. The factors that were responsible for the longer life of the cylindrical blocks are not known.

The shielded electrode design gave no improvement in moisture measurement under field conditions and has been eliminated from consideration. It did prove very useful, however, in laboratory tests in eliminating a source of variability in resistance blocks.

respective efficiencies in differentiating soil moisture levels. The data of table 9 have been assembled to cover these three points.

Standard errors of estimate are given in the first column of data. The error for tensiometers is based on one regression for the 1942 data, and is identical with the error of estimate that was given in table 2. The errors of estimate for plugs and blocks on Beltsville loam are based on separate regressions for each year (1942–1943) and are in effect, averages of the corresponding errors of estimate that are reported in table 5. The errors of estimate for plugs and blocks on Muirkirk sand are identical with those given in table 5. In each case the errors of estimate are based on the respective moisture ranges in which each type of instrument was found to be sensitive.

TABLE 9

Comparison of the utility of moisture instruments

INSTRUMENT	ERROR OF ESTIMATE	EFFECTIVE RANGE OF INSTRUMENT OPERATION							
		Moisture percentage scale				Available moisture scale			
		Lower limit*	Upper limit*	Net range	Efficiency of differentiation	Lower limit†	Upper limit†	Net range	Efficiency of differentiation
	pct.	*pct.*	*pct.*	*pct.*		*pct.*	*pct.*	*pct.*	
Beltsville silt loam									
Blocks..................	1.10	2.9	14.7	11.8	10.73	0	57.2	57.2	8.64
Plugs...................	0.89	8.8	18.5	9.7	10.90	21.7	80.1	58.4	10.90
Tensiometers...........	1.40	14.3	22.2	7.9	5.64	54.8	100.0	45.2	5.36
Muirkirk sand									
Blocks..................	0.56	0.8	5.5	4.7	8.39	0	29.1	29.1	4.46
Plugs...................	0.76	3.8	6.2	2.4	3.16	9.3	37.2	27.9	3.16

* These limits should be compared with a wilting point (pF 4.2) of approximately 5.2 per cent and a moisture equivalent of 21.8 per cent, for Beltsville silt loam. The wilting point for Muirkirk sand is about 3.0 per cent, the moisture equivalent 11.6 per cent.

† These limits should be compared with a wilting point of 0.0 per cent available moisture, and a moisture equivalent of 100.0 per cent available moisture.

The errors of estimate in table 9 show that on the Beltsville soil the gravimetric plugs gave the best performance of the three instruments. On Muirkirk sand the resistance blocks gave the lower estimate as judged by linear regressions; however, figure 7 indicates that linear regression does not fully satisfy the true plug reading-soil moisture relationships on Muirkirk sand between the limits of effective instrument operation. It appears, therefore, that whereas the experiment as a whole has tended to indicate a more consistent performance on the part of the gravimetric plugs (table 3) their performance is not better in all cases, and in any close evaluation, relative performance will be found to be at least partly dependent on the conditions of the test.

The lower limits of the respective ranges in which each type of instrument operated effectively are shown as soil moisture percentages in column 3, and the upper limits are given in column 4. The net ranges of the instruments appear in column 5. It is evident from these data that the errors of estimate alone are not an adequate basis for choice among the moisture instruments. The data on Beltsville silt loam show that the blocks and tensiometers are almost wholly non-competitive, since the upper limit of block operation coincides approximately with the lower limit of tensiometer operation. The plugs occupy an intermediate position between the two.

The net range in moisture percentage that is covered by any instrument is greatest for the resistance blocks on both the Beltsville and the Muirkirk soils.

When the net range is divided by the error of estimate[9] the efficiency of differentiation is obtained. These figures express the relative capabilities of the instruments to differentiate degrees of wetness within their respective moisture ranges. In this respect the tensiometers were considerably less effective than either the plugs or the blocks, since the latter instruments show the higher efficiencies of differentiation on the silt loam soil. The efficiency of the plugs was less than that of the blocks on Muirkirk sand.

The moisture-instrument ranges that have just been discussed include some data on resistance blocks that lie below the range of moisture that is available to plants. Similarly, they also include some data on tensiometers that lie above the normal field capacity of the Beltsville soil.

A comparison among the instruments is made in columns 7 to 10 on the basis of a scale of available moisture in which the wilting point has been set as 0.0 per cent and the moisture equivalent as 100.0 per cent of available moisture. The lower and upper limits of instrument operation have been set accordingly. The limits show that the plugs are sensitive in an intermediate range of available soil moisture and that the insensitive range also is divided into two levels of wetness.

The net ranges of available moisture that lie between the upper and lower limits of instrument operation show that the greatest range (58.4 per cent) is covered by the gravimetric plugs on the Beltsville soil. The operation of tensiometers was restricted to less than half of the available moisture range.

On Muirkirk sand both the blocks and the plugs operated over a limited range of moisture on both a moisture percentage and an available moisture scale. The reduction in range on the moisture percentage scale was to be expected because of the low water retention of Muirkirk sand, but the reduction in range on the available moisture scale is not so easily explained. It should be evident, however, from theoretical considerations that the basic responses of both instruments are determined by equilibriums that are established between the water that is held within the pores of the instrument unit and within the pores of the soil. Whenever too great a disparity exists between the pore characteristics of the two bodies, the moisture contents of the one cannot be matched by corresponding moisture contents in the other, and the lack of correlation

[9] See footnote 7.

must appear either as an increased error of estimate or as a decrease in the range of effective operation.[10]

The unsatisfactory character of the operation of both the plugs and blocks on Muirkirk sand is given expression in their efficiencies of differentiation for the available moisture range. In the opinion of the writers, it is doubtful whether an efficiency of differentiation of less than 6 would be of much practical value.

Acceptance of that limit would tend to rule out the use of tensiometers on the basis of the performance they gave in these tests. The blocks and plugs, on the other hand, did differentiate moisture levels effectively on the silt loam soil. In the available moisture range the gravimetric plug was notably better than the block in this respect.

Variability of soil moisture as determined by sampling

Soil moisture variability is a matter of some importance in any discussion of soil moisture measurement. Undoubted variations in soil moisture occur as a result of differences in soils, years, and cropping conditions, but since very little information appears to be available on the variability of soil moisture that occurs under similar conditions, it seems worth while to close this discussion of moisture measurement with an examination of the field variability in moisture that has been encountered.

In this connection it should be noted that the moisture plots were on areas that had been selected for uniformity. Evidence of nonuniformity was not wholly absent on either area and was the more marked on Muirkirk sand as judged by trial borings. The areas were as uniform, however, as could be found locally.

The variability in moisture that was found within plots has been indicated for segments of the total data by the standard deviations reported in tables 2 and 5. When the total data are considered, the standard deviation of moisture sampling amounted to 0.75 per cent on the Beltsville soil and 0.53 per cent on the Muirkirk soil. These standard deviations include both the real differences in soil moisture on different parts of a single plot and whatever errors may have existed in making the determinations.

The maximum ranges in mean seasonal differences in soil moisture that were found between replicated plots are shown in columns 4 and 5 of table 10. The

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[10] Tests of plugs and blocks that were known to have the same porosity characteristics showed that the differences in range that were exhibited by two instruments on one soil were not due to differences in porosity, but were probably due to differences in sensitivity between the resistance and gravimetric methods of measurement.

It seems probable, however, that the gravimetric plugs could be improved, and adapted better to specific soil porosities, by making them of some material of more desirable pore characteristics than can be obtained from gypsum casts, also by making them in several grades. Richards and Weaver (14) have used ceramic sorption blocks successfully to avoid the solubility effects and the lack of mechanical strength of gypsum.

The same probability is not evident in the case of the resistance blocks. A semisoluble material having ionic properties is necessary for resistance block construction to buffer the effects on conductivity of variable soil electrolyte concentrations.

TABLE 10

Analyses of variance of soil moisture determinations by random sampling

COVER	YEAR	RANGE OF PLOT MEANS			Between plots†			Error A: Plots × dates interaction‡			Error B: Sampling error between duplicate samples‡		
		Number	High	Low	Df	Sum of squares	Mean square	Df	Sum of squares	Mean square	Df	Sum of squares	Mean square
Beltsville silt loam													
Bluegrass	1941	9	11.90	10.11	8	90.1312	11.2664**	136	303.0938	2.2286**	162	237.4969	1.4660
Bluegrass	1942	12	15.72	14.17	11	123.4459	11.2224**	264	378.5192	1.4338**	300	296.6682	0.9889
Rye grass	1943	3	11.53	10.84	2	9.6591	4.8296	38	61.3063	1.6133	60	84.7491	1.4125
Bare uncultivated	1943	3	15.40	14.36	2	24.2969	12.1484**	38	49.4482	1.3023	60	54.5383	0.9090
Bare cultivated	1943	3	16.78	16.24	2	6.4256	3.2128	38	51.8144	1.3635*	60	43.5220	0.7254
Straw mulch	1943	3	18.84	17.87	2	22.1971	11.0986*	38	86.4706	2.2755*	60	77.0257	1.2838
Muirkirk sand													
Rye grass	1943	3	5.71	4.80	2	17.3076	8.6538**	38	24.9604	0.6568	60	30.7659	0.5128
Bare cultivated	1943	3	6.92	5.88	2	22.6545	11.3272**	38	21.9986	0.5789	60	32.4219	0.5404
Straw mulch	1943	3	8.20	6.46	2	63.6549	31.8274**	38	27.3887	0.7208	60	37.6181	0.6270

* Significant at 5 per cent level.
** Significant at 1 per cent level.
† Significance based on "Error A."
‡ Significance based on "Error B."

range of moisture in any group of plots is less than 2 per cent, yet these differences are shown to be significant or highly significant in most cases by analyses of the between-plot variances. Moreover, the significance that is found in four cases of the plot $\times$ dates interactions shows that these replicates not only maintained different average levels of soil moisture, but were also inconsistent in their individual response to conditions that were associated with dates of sampling.

Differences in moisture levels that relate to years and covers were to be expected, and are evident in columns 4 and 5. The figures for the grassed plots substantiate statements that have been made previously with respect to the relative wetness of the 1942 season. The 1943 data allow some comparison of moisture differences that were induced by management or cover. Most noteworthy perhaps is the higher level of moisture that is maintained by cultivation as opposed to no cultivation on the bare plots of the silt loam soil. The difference in level is significant as judged by the T test.

The variation that is characteristic of soil moisture under similar conditions is involved in the errors of estimate of the moisture-measuring instruments, for it will be recalled that the moisture samples were taken in 6-foot squares about the instrument locations.

Actually, therefore, the instrument may be expected to give the day-to-day trends in soil moisture at a fixed location and throughout its sensitive range with a greater accuracy than that shown by the error of estimate.

In order to obtain a close approximation of the average moisture content of larger areas, such as entire fields, a considerable number of replicate instruments would be required, because of moisture variability. Unless these are provided, small differences in errors of estimate would seem to be a poor basis for choice among the instruments, and their utility would depend to a greater degree upon their range and efficiency of differentiation.

SUMMARY AND CONCLUSIONS

Comparisons have been made under field conditions of the behavior of three types of moisture-measuring instruments: tensiometers, resistance blocks, and gravimetric plugs. The performances of the instruments were judged by moisture determinations on soil samples that were taken at random within a restricted area around each instrument installation.

The three instruments were found to be different with respect to the accuracy with which they measured soil moisture, the ranges of moisture in which the instruments were sensitive, and their efficiencies in differentiating soil moisture levels.

On a silt loam soil the plugs and blocks were superior to the tensiometers with respect to errors of estimate and range of operation, but were insensitive to moisture changes in a range of higher moisture contents where the tensiometers gave their best performance.

On a silt loam soil the plugs were better than the blocks with respect to errors of estimate, efficiencies of differentiation, and *location* of their sensitive ranges on an available moisture scale.

On a very sandy soil the blocks appeared to be better than the plugs in all respects, although the performance of neither instrument was satisfactory throughout the available moisture range.
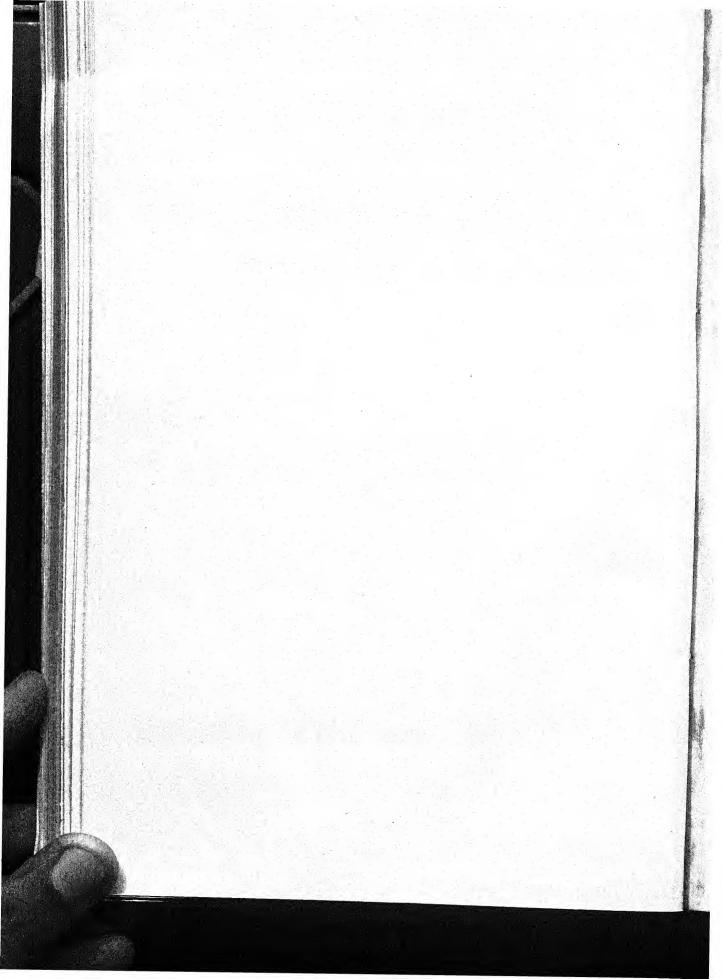
The results of the experiment as a whole indicate clearly that no one instrument is "best" in its present state of development. The choice of method for measuring soil moisture should be based on differences in the conditions of measurement as well as on instrument characteristics. It is the opinion of the writers that tensiometers are decidedly limited in usefulness, that under a majority of soil conditions gravimetric plugs are best adapted to accurate measurement, and that resistance blocks are best adapted to semiquantitative measurements of the variable field moisture of large areas under conditions that do not require the improved accuracy that can be obtained by temperature corrections.

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MICROORGANISMS AND SOIL AGGREGATION: II. INFLUENCE OF BACTERIAL POLYSACCHARIDES ON SOIL STRUCTURE[1]

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During the microbiological decomposition of organic residues, soil-aggregating substances are produced (1, 8, 17). These consist of the microbial bodies themselves, decomposition products, and synthesized substances (5, 6, 7, 10, 11, 15). In a previous study (9) a polysaccharide synthesized by a soil bacillus was found to be an effective soil-aggregating agent. The investigations reported in the present paper were undertaken to determine the influence of a variety of bacterial polysaccharides on soil structure.

EXPERIMENTAL

Methods

The soil used was Declo loam collected near Aberdeen, Idaho. It consisted of 46 per cent sand, 41 per cent silt, 13 per cent clay, and contained 1.46 per cent organic matter. The pH was 8.0 and the moisture-holding capacity 40 per cent. The aggregating effect of various treatments on the silt and clay particles ($< 50 \mu$) was determined by a pipette method (9). The degree of aggregation is reported as the percentage by weight of the total silt plus clay particles that are bound into water-stable aggregates larger than 50μ in diameter. Before analyses all samples were dried at 50°C. and passed through a 4-mm. sieve. An additional estimation of the stability of the soil structure was obtained by placing in duplicate approximately 10-gm. lumps of the treated soil on a screen (1 sq. cm. openings) suspended in water, and determining the average length of time required for the lumps to disintegrate and pass through. This is referred to as "slaking time."

Selection of cultures and preparation of polysaccharides

Six bacteria, which were known to synthesize polysaccharides or were found by laboratory tests to produce them, were selected. Two strains of *Bacillus subtilis* were used: one was isolated from a southern Idaho soil and is the same one reported in a previous study (9); the other, *B. subtilis* Cohn, was obtained from the American Type Culture Collection. A culture of the acid-tolerant nitrogen-fixer, *Azotobacter indicum*, was obtained from Dr. Robert L. Starkey of the New Jersey Agricultural Experiment Station. Two capsulated bacteria, a Gram-negative rod referred to as "organism 1," and a Gram-positive, non-

sporeforming rod referred to as *"Bacterium* sp.," were isolated from Palouse silt loam which had been in grass sod for 20 years. *Leuconostoc dextranicum* was obtained from the American Type Culture Collection.

For production of polysaccharide, the *B. subtilis* sp. and *A. indicum* were grown in a liquid synthetic medium containing sucrose as the carbon and energy source, NaNO₃ as the nitrogen source, and other inorganic salts. *B. subtilis* Cohn did not grow when inorganic nitrogen was used as the nitrogen source. For this reason asparagine was substituted for the NaNO₃ in the case of this organism. The two soil isolates grew very poorly in liquid medium and were therefore cultured on solid sucrose-NaNO₃ medium.

Briefly, the polysaccharides were obtained by centrifuging to get rid of the cells, dialyzing, concentrating under reduced pressure, and precipitating the polysaccharides in alcohol. If considerable nitrogen was still present, the preparations were dissolved in NaOH solution, heated over a hot water bath, dialyzed, treated with a protein precipitant, centrifuged, again dialyzed, concentrated

TABLE 1

Chemical properties of some polysaccharides synthesized by soil bacteria

SOURCE OF POLYSACCHARIDE	ASH	ORGANIC CARBON*	NITRO-GEN†	URONIC ACIDS‡	NATURE OF POLYSACCHARIDE
	per cent	*per cent*	*per cent*	*per cent*	
B. subtilis Cohn.......................	0.74	43.3	0	tr.	Fructosan
B. subtilis sp.........................	1.82	43.4	0.04	3.1	Fructosan
A. indicum............................	4.28	40.5	0	4.9	Fructosan
Organism 1.............................	4.64	39.7	0	6.0	Dextran
Bacterium sp..........................	4.71	42.5	0	14.4	Dextran
L. dextranicum........................	2.63	43.6	1.52	tr.	Dextran

* Digestion with chromic acid and titration with standard ferrous ammonium sulfate.
† Kjeldahl method.
‡ Slight modification of Dickson's method (3).

under reduced pressure, and the polysaccharides precipitated in alcohol. Slight variations were necessary with each organism. The precipitated preparations were treated with absolute alcohol, followed by ether, and dried in a forced convection oven at 50°C.[3]

L. dextranicum was cultured and the dextran obtained essentially according to the method of Hassid and Barker (4).

Nature of polysaccharides

Some chemical properties of the bacterial polysaccharides are reported in table 1. The type of polysaccharide synthesized was determined by hydrolyzing with 2 per cent HCl, preparing and purifying osazones, taking melting points of osazones, measuring optical rotation, and making the Seliwanoff test.[4]

[3] The details of these procedures and a description of the polysaccharides obtained will be reported in another publication.
[4] The details of these tests will be reported elsewhere.

The polysaccharide synthesized by *B. subtilis* sp. in the sucrose-NaNO₃ medium, with the exception of a small amount of uronic acid, is apparently the same as the levan (12) synthesized by *B. subtilis* Cohn, which would not grow in the liquid NaNO₃ medium. *Azotobacter indicum* also synthesized a fructosan; however, its physical properties and its influence on soil structure were quite different from those of the levan from *B. subtilis*. The polysaccharide from *A. indicum* also contained a small amount of uronic acid.

The two organisms isolated from the soil both synthesized dextrans containing uronic acid units.

TABLE 2

Growth* of polysaccharide-synthesizing bacteria on carbohydrate-NaNO₃ media

CARBOHYDRATE	AZOTOBACTER INDICUM	ORGANISM 1	BACTERIUM SP.
Lactose	−	−	++++
Sucrose	++++	++++	++++
Glucose	+++	+++	++++
Raffinose	+++	++++	++++
Mannose	+++	++	++++
Maltose	−	++	++++
Galactose	−	++	++++
Fructose	−	−	++++
Xylose	+	+	+
Arabinose	+++	++++	+
Inulin	+	+	++++
Dextrin	++	+++	++++
Mannite	−	++++	++++
Grass–alfalfa-hay extract	++++	++++	++++
Grass–alfalfa-root extract	++++	++++	++++
Wheat-straw extract	+++	++++	++++
Alfalfa-hay extract	++++	+++	++++

* − No growth.
  + Trace.
  ++ Poor growth.
  +++ Good growth.
  ++++ Heavy growth.

Growth on various media

Bacillus subtilis sp. when first isolated from the soil produced a polysaccharide from sucrose, glucose, maltose, xylose, and arabinose. Upon incubation on artificial media it quickly lost its ability to synthesize polysaccharide in significant amounts in all except the sucrose medium.

The ability of *A. indicum* and the two soil isolates to grow and produce slimy capsular material from various energy and carbon sources was investigated. The organisms were grown on synthetic solid media similar to the one used for large-scale production of the polysaccharides. Results were observed after 3 and 7 days' incubation and also after 2 weeks' incubation in case of *A. indicum*.

The carbon sources investigated and the results obtained are presented in table 2. *Bacterium* sp. produced a heavy, milky growth on all media except the

two pentoses, xylose and arabinose. Organism 1 did not utilize xylose to any extent but made heavy slimy to butyrous growth on arabinose medium. Lactose, mannose, inulin, and fructose were not readily attacked. *Azotobacter indicum* apparently was able to utilize to a great extent only sucrose, mannose, raffinose, glucose, arabinose, dextrin, and the extracts from complex organic materials. In all cases growth was very slimy or viscid.

It should be pointed out that all three of these organisms grew well and produced slimy capsular material from extracts of plant residues. This would indicate that they very likely produce these substances in the soil.

Influence of polysaccharides on soil structure

The effect of various concentrations of the polysaccharides on the structure of Declo loam is reported in table 3. For this study the preparations were dissolved in water and placed in large evaporating dishes. The soil was then carefully added to the dishes. This procedure was necessary because some of the preparations were very thick and viscid and would not penetrate the soil if added to the surface. The fructosan from *A. indicum* and the dextran from *Bacterium* sp. went into solution with difficulty. For this reason the influence of the latter on the soil was determined both before and after it was precipitated in alcohol and obtained in the dry state. The concentration of fructosan from *A. indicum* before precipitation was so small that a similar procedure could not be carried out with this material.

All of the polysaccharides were markedly effective soil-aggregating agents. As little as 0.1 gm. of polysaccharide in 100 gm. of soil brought about from 44 to 70 per cent aggregation of the silt and clay particles compared to 28 per cent for the control. The levan from *B. subtilis* was least effective and the dextran from *Bacterium* sp. most effective. Only 0.6 per cent concentration of this latter material resulted in an 87 per cent aggregation of the silt and clay particles, and a 10 gm. lump of the treated soil required 2 days in water to disintegrate sufficiently to pass through a screen with 1 sq. cm. openings. The efficiency of the polysaccharides in aggregating the silt and clay particles was greatest in the 0.1 per cent concentration. For example, 0.1 gm. of the dextran from *Bacterium* sp. aggregated 22.8 gm. of dispersed silt + clay. As the concentration and consequently the aggregation increased it became more and more difficult to aggregate the remaining dispersed silt and clay. At 1 per cent concentration the same dextran aggregated only 3.9 gm. of dispersed silt + clay for each 0.1 gm. of the material. The effect of this polysaccharide on slaking of aggregates is shown in figure 1. The picture was taken approximately 1 hour after water was added.

The aggregating effect of the bacterial polysaccharides in combination with protein and lignin was next studied. Casein was used for the protein. The lignin was alkali lignin from white pine and was prepared by Dr. E. V. White of the Forestry Department at the University of Idaho. Before use, it was brought into solution by the addition of one or two drops of NH_4OH to a suspension in water and heating. The dextran from *L. dextranicum* and the fructosan from *B. subtilis* Cohn were not used for this study.

TABLE 3

Influence of various concentrations of bacterial polysaccharides on aggregation and slaking of Declo loam

POLYSACCHARIDE	CONCENTRATION	WEIGHT DISPERSED SILT + CLAY	AGGREGA-TION	SLAKING TIME	DISPERSED SILT + CLAY AGGREGATED PER 0.1 GM. POLYSAC-CHARIDE
	per cent	*gm.*	*per cent*	*seconds*	*gm.*
	Dispersed soil	54.4	0	. . . . .	. . . .
	Control	39.2	28	13	0
Sucrose	0.3	39.7	27	11	0
	0.6	38.6	29	15	0
Fructosan from *B. subtilis* Cohn	0.1	30.5	44	15	8.7
	0.3	26.4	51	18	4.3
	0.6	21.4	61	23	3.0
	1.0	18.3	66	30	2.1
Fructosan from *B. subtilis* sp.	0.1	30.3	44	15	8.9
	0.3	26.1	52	25	4.4
	0.6	20.1	63	22	3.0
	1.0	16.2	71	29	2.3
Fructosan from *A. indicum*	0.1	22.7	59	25	16.5
	0.3	19.0	65	180	6.7
	0.6	14.7	73	6*	4.1
	1.0	6.9	87	25*	3.2
Dextran from organism 1	0.1	22.0	60	12	17.2
	0.3	20.4	63	76	6.3
	0.6	15.6	71	120	3.9
	1.0	13.1	76	1,680	2.6
Dextran from *Bacterium* sp. (before precipitation in alcohol)	0.1	16.4	70	300	22.8
	0.3	13.8	75	4*	8.5
	0.6	7.1	87	48*	5.7
	1.0	6.8	88	3†	3.9
Dextran from *Bacterium* sp. (after precipitation and drying)	0.1	29.6	46	35	9.6
	0.3	23.8	57	55	4.5
	0.6	20.4	63	960	3.1
	1.0	15.8	71	3,900	2.3
Dextran from *L. dextranicum*	0.1	24.0	56	15	15.2
	0.3	18.6	66	32	6.8
	0.6	14.8	74	38	4.1
	1.0	13.4	75	180	2.6

* Hours.
† Days.

The results are recorded in table 4. Before incubation, lignin alone was less effective in aggregating the soil than were any of the polysaccharides. Casein was just as active as the fructosan from *B. subtilis* sp. but less active than the other preparations. Fructosan from *B. subtilis* and dextran from *Bacterium* sp. alone brought about slightly greater aggregation than together with lignin or casein. The dextran from organism 1 in combination with lignin was just as effective as when used alone, but together with casein it was less active. On the other hand, the fructosan from *A. indicum* in combination with casein brought about considerable aggregation, but together with lignin its effectiveness decreased markedly. The depressive effect of lignin on the binding power of this polysaccharide-casein combination is also shown in the length of slaking time. After 6 days in distilled water a lump of the latter still held its shape. When lignin was present, the lump disintegrated in less than 2 minutes. From the point of view of slaking time, all other polysaccharide-casein-lignin com-
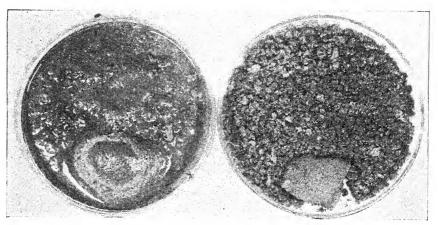
FIG. 1. SLAKING OF AGGREGATES AND LUMPS OF DECLO LOAM

Left, no treatment; right, treated with 0.6 per cent dextran from soil bacterium.

binations greatly increased the stability of the soil structure. For example, the slaking time for casein alone was 3 minutes, for lignin 2 minutes, and for fructosan from *B. subtilis* 25 seconds. For a combination of the three it was over 6 days. It will be noted from table 3 that the greatest slaking time for a 1 per cent concentration of a bacterial polysaccharide was 3 days.

After 30 days' incubation under favorable moisture conditions only slight to moderate changes in aggregation had occurred. Aggregation of the soil treated with fructosan from *B. subtilis* changed very little. All other polysaccharide treatments and the casein treatment showed slight decreases. The aggregation of the soil treated with lignin alone and with the mixture of lignin and fructosan from *A. indicum* increased substantially. That treated with the other lignin-polysaccharide combinations changed very little.

For comparison with the polysaccharide, casein, and lignin treatments, soil portions were incubated with 0.3 and 0.6 per cent concentrations of sucrose. The

TABLE 4

Effect of bacterial polysaccharides, protein, and lignin on aggregation and slaking of Declo loam

TREATMENT	BEFORE INCUBATION			AFTER 30 DAYS' INCUBATION		
	Weight dispersed silt + clay	Aggregation	Slaking time	Weight dispersed silt + clay	Aggregation	Slaking time
	gm.	per cent	seconds	gm.	per cent	seconds
Control.................................	39.1	28	11	37.1	32	15
Sucrose, 0.3%............................	39.7	27	11	29.9	45	......
Sucrose, 0.6%............................	38.6	29	15	24.0	54	......
Casein, 0.3%.............................	24.1	56	120	26.6	51	20
Casein, 0.6%.............................	20.4	62	180	20.0	63	120
Lignin, 0.3%.............................	32.1	42	90	24.8	54	1,200
Lignin, 0.6%.............................	26.2	52	120	19.7	64	4†
Lignin + casein, 0.3% each.............	25.9	52	540	17.5	68	2†
Fructosan from *B. subtilis*, 0.3%........	26.1	52	23	25.3	54	30
Fructosan from *B. subtilis*, 0.6%........	20.1	63	25	19.5	64	120
Fructosan from *B. subtilis* + casein, 0.3% each.....................	22.3	59	180	24.0	56	30
Fructosan from *B. subtilis* + lignin, 0.3% each.....................	22.8	58	1,500	17.6	68	3†
Fructosan from *B. subtilis* + lignin + casein, 0.3% each.....................	14.7	73	>6*	12.2	78	6†
Fructosan from *A. indicum*, 0.3%.......	19.0	65	180	25.9	52	25
Fructosan from *A. indicum*, 0.6%.......	14.7	73	6†	23.1	58	30
Fructosan from *A. indicum* + casein, 0.3% each..................................	13.3	76	>6*	19.5	64	25
Fructosan from *A. indicum* + lignin, 0.3% each..................................	24.6	55	75	19.6	64	240
Fructosan from *A. indicum* + lignin + casein, 0.3% each.....................	22.7	58	90	14.6	73	3†
Dextran from organism 1, 0.3%.........	20.4	63	76	24.4	55	20
Dextran from organism 1, 0.6%.........	15.6	71	120	21.6	60	240
Dextran from organism 1 + casein, 0.3% each..................................	21.5	61	180	20.1	63	60
Dextran from organism 1 + lignin, 0.3% each..................................	14.7	73	2†	16.8	69	2,100
Dextran from organism 1 + lignin + casein, 0.3% each.....................	12.6	77	7†	12.0	78	3†
Dextran from *Bacterium* sp. 0.3%.......	13.8	75	4†	20.5	62	75
Dextran from *Bacterium* sp. 0.6%	7.1	87	2*	18.9	65	48
Dextran from *Bacterium* sp. + casein, 0.3% each..................................	13.3	76	9†	17.5	68	24
Dextran from *Bacterium* sp. + lignin, 0.3% each..................................	13.1	76	4†	17.1	68	2,100
Dextran from *Bacterium* sp. + lignin + casein, 0.3% each..................	11.3	79	4*	14.1	74	2,760

* Days.
† Hours.

resulting aggregation after 30 days was 40 and 54 per cent, respectively. Though considerable, this influence was less than any of the polysaccharide, lignin, and casein treatments. Before incubation sucrose had no effect (table 3).

Utilization of polysaccharides by microbes

A study was made of the ability of various microbes to utilizes the bacterial polysaccharides as a carbon and energy source. The different preparations were incorporated into a synthetic agar medium. Plates were poured and streaked with a large number of soil microbes consisting of bacteria, actinomycetes, and fungi. The extent of growth developing upon incubation compared with that on glucose agar plates and on media containing no carbohydrate was observed.

With the exception of the actinomycetes, the best growth in every instance occurred on the glucose medium. From the broad point of view, all the poly-saccharides were much less available to the microorganisms under consideration than was glucose. In every instance, however, there were at least one or two organisms apparently capable of utilizing the polysaccharide to a considerable extent. The actinomycetes made good growth on all the media. Among the fungi, *Hormodendrum* was able to utilize the greatest number of polysaccharides, the dextran from organism 1 being the only preparation on which it failed to grow. Among the bacteria, *Pseudomonas* sp., *Bacterium* sp., and *Bacillus subtilis* were most active. The dextran from organism 1 was apparently the most resistant to microbial attack. Only the actinomycetes were apparently able to utilize this material.

DISCUSSION

A variety of polysaccharides synthesized by soil bacteria brought about very marked aggregation of Declo loam. The polysaccharides consisted of three fructosans and three dextrans containing varying amounts of uronic acid. The effectiveness of the preparations did not depend on the structural units (sugars) involved. A dextran from the soil bacterium produced the most stable struc-ture, whereas fructosan from *Bacillus subtilis* was least effective. On the other hand, fructosan from *Azotobacter indicum* brought about greater aggregation than the other two dextrans.

In general, the bacterial polysaccharides were better aggregating substances than was casein or lignin. It will be recalled that the lignin in this study was brought into solution before it was added to the soil. When incorporated with soil in the insoluble or dry state it has little effect on soil structure (7). When combined with casein and lignin, the polysaccharides, with minor exceptions, were just as effective as alone. After the polysaccharides were incubated for 30 days, their aggregating influence had changed but slightly or had decreased. In combination with casein and lignin, they induced little change or an increase in aggregation. After incubation of the sucrose-treated soil, the aggregation was considerable but was less than that resulting from any of the polysaccharide or polysaccharide, casein, and lignin treatments. Since sucrose, as such, has little influence on soil structure, the effect after incubation resulted from the production of soil-binding substances by the microbes decomposing it.

It is probable that part of the aggregation in the polysaccharide-treated soil resulted from undecomposed material and part from new binding substances produced by microbial decomposition or transformation of the original organic materials. Although the polysaccharides constituted a very poor energy and carbon source for most microbes tested, there was at least one organism in each case capable of utilizing them. In soil there are probably others.

It is also quite possible that the polysaccharides, casein, lignin, and inorganic colloids undergo physicochemical combinations resulting in the formation of complexes more or less resistant to decomposition. This would be expected especially in the case of the polysaccharides containing the active uronic acid groups. The bulk of soil humus consists of lignin-derived substances, nitrogenous complexes, and polysaccharides. It has been demonstrated that generally 10 to 30 per cent of the soil humus consists of polyuronides (14, 16). Notwithstanding this fact, the author knows of no naturally occurring polysaccharide which, when obtained in the pure state, is not attacked by at least one or more microorganisms. Plant polysaccharides are readily destroyed in the soil (17). It is very likely that the polysaccharide portion of soil humus is largely microbially derived (13) and that its persistence in the soil is due to its combination with other soil constituents which render it resistant to decomposition. In such a combination it very probably contributes to so-called stable soil structure.

As well as contributing to stable soil structure, microbial polysaccharides undoubtedly play an active rôle in what might be termed "passive" soil structure. This is the greatly increased aggregation which occurs when undecomposed plant residues or organic substances are incorporated into the soil. Maximum aggregation is usually reached within 3 to 20 days' incubation under favorable conditions of moisture and temperature (2, 7, 8, 11), after which it decreases until a state of equilibrium is reached. The high aggregation is brought about largely by microbial cells, decomposition products, and synthesized substances, some of which are polysaccharides. These active materials are themselves slowly or rapidly destroyed, and as a result, aggregation decreases. It would be expected that the polysaccharides composed entirely of straight sugar groups would undergo more or less complete decomposition, and thus their aggregating effect would be completely passive in nature. On the other hand, those containing the active uronic acid groups or those linked with nitrogenous complexes would be expected to undergo physicochemical reactions with other active substances in the soil and in some instances become resistant to further decomposition. Should such occur, it is probable that only a small percentage of the total produced would be stabilized in this manner. However, under conditions of a continuous supply of organic material, such as occurs under sod, the cumulative total of stabilized polysaccharide would be considerable.

With respect to the marked aggregation present after 30 days' incubation in the treated soil portions, it is not possible to say how much was due to unaltered original components and how much to new aggregating substances resulting from microbial decomposition. Carbon dioxide evolution studies during incubation would do much to elucidate the matter.

SUMMARY

Six bacterial polysaccharides, three fructosans and three dextrans, were prepared in quantity and their influence on soil aggregation and slaking was determined. The effectiveness of the different preparations varied but was very marked in all cases. The polysaccharides alone had a greater influence than the casein or lignin. In combination with lignin and casein, they influenced soil structure just as beneficially as when used alone.

The bacterial polysaccharides, in general, were attacked to a limited extent by microorganisms. However, at least one and usually several microbes were capable of utilizing each.

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DYNAMICS OF WIND EROSION: IV. THE TRANSLOCATING AND ABRASIVE ACTION OF THE WIND[1]

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In a previous paper (4) factors influencing the transport capacity of the wind were reviewed and their relative influence on erosion of the soil was indicated. The capacity of the wind to transport soil material is only one of the two types of wind action on soils. In addition, clods and other more or less indurated materials are continually being disintegrated or abraded as a result of impacts of soil grains that are being transported by the wind. The disintegration of clods and surface crust is effected to some degree by the general weather conditions and by cultivation, and the wind merely removes the fine and loose soil material, but under certain conditions it is possible for the wind to attack and wear away the surface crust and abrade even the hardest rocks.

Literature, particularly that in the field of geology, is replete with examples of the importance of abrasive action of wind-borne sand particles as an agent of physical disintegration of rocks and of soil formation. The abrasive action of flying sand on glass and metal is generally familiar, and the sand blast, which is based on this principle, is a method that is widely used in various branches of industrial work.

The object of the study outlined in this paper was to learn what influence the abrasive action has on the intensity of wind erosion and to find what effect areas susceptible to erosion have on the erosiveness of the adjacent wind-resistant soil. In order to show clearly the importance of wind action on soils, it was necessary to study the manner of its action in a wind tunnel in greater detail than has been possible so far in this series of experiments.

METHOD OF PROCEDURE

A weighed amount of soil was spread over the tunnel floor to an average depth of 2.5 inches, and a moderate wind was turned on for the length of time required to remove from the surface all particles that were erosive under that particular velocity. After complete cessation of drifting and without change in the velocity of the wind, fine dune sand was fed at the rate of 0.26 gm. per centimeter width per second on the windward end of the soil area. The loss or gain in the weight of the soil at definite intervals after exposure to this "sand blast" action was recorded.

In another experiment, six widely different soils were worked at three different moisture contents and immediately packed into containers at a pressure of 4

pounds per square inch.   The moisture contents at which the soils were packed
were those of the lower plastic limit, the upper plastic limit, and halfway between
the two.   The lower and the upper plastic limits were determined according to
the technique of Russel and Wehr (7).   After slow and thorough drying, the
samples, each in the form of a cylindrical block, were removed from the con-
tainers.   They were then exposed to direct abrasion by various drift soils and
dune sand blown in a narrow stream against the blocks under a moderate wind.
The loss in the weight of the exposed block was taken as a measure of the relative
susceptibility of the soils to abrasion.   The drift soils used as abrasors represent
that part of the soil which had been moved about by the wind and deposited in
mounds next to various obstructions, either within the eroded fields or on adja-
cent land.   These drifted soils were composed of grains ranging from 0.1 to
1 mm. in diameter.

RESULTS

Effect of abrasive and extrusive action of wind-borne sand particles

On exposure of a soil to wind, a movement began on the part of some grains
the threshold velocity of which was equal to or lower than the actual velocity
of the wind.   The removal continued for some time and ceased as soon as the
surface became covered with a bed of grains and clods too coarse to be moved by
the wind.   Introduction of fine dune sand on the windward side of the soil area,
without change in the velocity of the wind, brought about renewal of soil move-
ment, which then continued indefinitely.   The rate of soil removal by the wind
laden with sand was very rapid at first but diminished quickly with duration of
exposure and finally reached a constant rate.   Table 1 indicates the amounts of
soil that were removed by wind alone and the rates of subsequent removal by
wind laden with sand.   All soils were highly resistant to erosion by wind alone
but drifted readily under the bombarding action of dune sand.

Two important ideas are suggested by this experiment:

1. The movement of soil by wind is initiated as a result of the pressure of the
wind against the grains.   After being rolled a short distance by the wind, the
grains suddenly leap into the air and form the initial stage of movement in
saltation.   They gain considerable forward momentum from the pressure of
the wind and descend at a much greater speed than their initial upward velocity.
On striking the surface, they may rebound and continue their movement in
saltation or, as a result of impact, cause other grains to move along the surface
of the ground or rise into the air, themselves becoming buried in the loose surface
or forming part of the movement in surface creep.   Irrespective of whether the
movement of these fine grains is initiated by the direct pressure of the wind or
by impact of descending grains, their rate of removal is wholly dependent on the
pressure of the wind up to the height of saltation.   This form of erosion, which
is manifested mainly by movement in saltation, will henceforth be designated
as *effluxion.*

2. The erosion of the soil by effluxion gives rise to at least several other forms

of erosion. The bombarding action of the grains whose movement is brought about by the pressure of the wind against them causes the movement of coarser, less erosive grains, which, under the same wind velocity, but without such bombardment, would remain at rest. But the movement of these difficultly erosive fractions is limited by the quantity of grains moved by effluxion. The results of the experiment just outlined show that removal of grains by effluxion proceeds relatively rapidly and, especially on an area of limited length, may be completed before the removal of the coarser, less erosive grains has been accomplished. Hence the amount of erosion on a particular area is limited by the quantity of grains that are moved across it by effluxion. With a supply of highly erosive grains from the windward, all of the difficultly erosive grains may finally be removed and the subsequent rate of soil removal from a particular area would

TABLE 1

Erosion of soil by wind without sand and laden with sand

SOIL TYPE	WIND VELOCITY AT 12-INCH HEIGHT	AMOUNT OF SOIL REMOVED BY WIND	
		Without sand*	With sand†
	m.p.h.	*gm./sq.m.*	*gm./sq.m./min.*
Hatton fine sandy loam..............	18.4	0.45	11.15
	22.0	0.61	13.05
Haverhill loam......................	16.3	0.97	7.45
	22.0	1.49	11.49
Cypress clay loam...................	15.7	0.01	7.37
	22.0	0.21	11.60
Fox Valley silty clay loam...........	19.8	0.18	2.74
	22.0	0.48	5.29
Sceptre clay........................	22.0	0	0.50

* Amounts removed up to the time soil drifting ceased.
† Rates of soil removal after cessation of removal by wind without sand.

then depend entirely on the relative susceptibility of the surface crust and clods to the disintegrating action of the wind-borne grains. The amount of erosion shown in the last column of table 1 is therefore due to two forms of erosion acting simultaneously: first, removal of the grains movable under the bombarding action of sand grains carried by effluxion; and second, wearing away of all more or less indurated materials. The first form of erosion will be termed *extrusion*; the second, *abrasion*.

The soils in the form of cylindrical blocks showed a very wide degree of susceptibility to abrasion by dune sand (fig. 1). The coarser the texture, the more susceptible was the soil to abrasion, with the exception of Haverhill clay loam. The high lime content of Haverhill clay loam was responsible for its relatively high susceptibility to abrasion. The susceptibility of the different soils to this

form of erosion ranged from a relative value of 1 to 30. Figure 2A indicates more clearly the extent to which the different soils were abraded by dune sand.

As shown in figure 1, the relative susceptibility of the various soils to abrasion varied markedly with the moisture content at the time they were packed. When packed at the lower plastic limit, the soils were at least seven times as susceptible to abrasion as when they were packed at the upper plastic limit. The increase in compactness of clods formed as a result of packing apparently decreased the susceptibility of the soils to abrasion. These results show that puddling or packing soils in a moist condition in the field should have a considerable effect in increasing their resistance to this form of wind erosion.
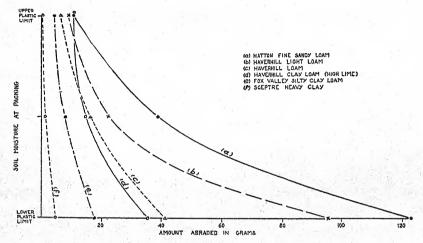
FIG. 1. SUSCEPTIBILITY OF VARIOUS SOIL TYPES TO ABRASION BY DUNE SAND

Four hundred grams of sand was blown against dry soil blocks prepared at three different moisture contents.

Relative abrasive action of different soil materials

Dune sand was most abrasive on all soils, followed in order by Sceptre heavy clay drift, Hatton fine sandy loam drift, Cypress loam drift, and pulverized loam containing much dust less than 0.1 mm. in diameter (fig. 3). The relatively low abrasive action of the Cypress loam drift, and particularly of the pulverized loam, was apparently due to a high content of dust which exhibited no abrasive action; whereas the relatively high disintegrating action of blown dune sand was evidently due to the absence of dust, the higher specific gravity of the sand grains, and their sharper edges. Figure 2B, indicates the nature and extent of abrasion caused by the different soil materials. The relative order of the susceptibility of the different soils to abrasion remained approximately the same, irrespective of the type of soil material that was used as abrasor.

Further work was undertaken to obtain specific information on the relative effect of the different types of abrasors on the exposed soil. Table 2 indicates the susceptibility of Haverhill loam to abrasion by various types of individual soil particles and aggregates varying widely in texture and size. The data

indicate that soil particles less than 0.05 mm. in diameter had no abrasive action on the soil but, rather, stuck to the surface of the soil, causing an increase in weight. The larger the quantity of fine dust contained in the blown material,
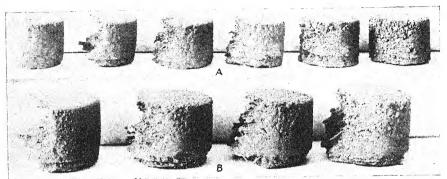
FIG. 2. NATURE AND EXTENT OF ABRASION ON DIFFERENT SOILS PACKED AT THE LOWER PLASTIC LIMIT

Wind direction left to right.

A. (Left to right) Hatton fine sandy loam, Haverhill light loam, Haverhill clay loam (with high lime), Haverhill loam, Fox Valley silty clay loam, and Sceptre heavy clay, each abraded by 400 gm. of dune sand.

B. Haverhill light loam abraded by 400 gm. of (left to right) dune sand, Sceptre heavy clay drift, Hatton fine sand loam drift, and Cypress loam drift during 2 minutes of exposure under a 30-mile-per-hour wind.
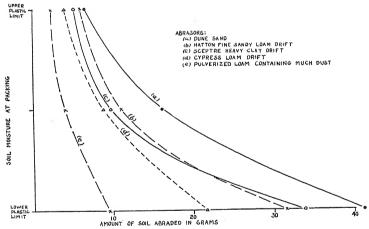
FIG. 3. EFFECT OF DIFFERENT ABRASORS ON DRY BLOCKS OF HAVERHILL LOAM

Four hundred grams of abrasors was blown against the blocks prepared at three different moisture contents.

the greater was the increase in the weight of the exposed soil. It has been shown previously (3) that fine dust is extremely resistant to erosion by wind. The high resistance to erosion and the negative abrasive action of the fine soil particles are apparently due, in part, to one and the same cause—their relatively

high cohesion. The data also show that sand particles cause a greater degree of abrasion of soil than the same sized clay particles, but the greater the size, the smaller is the difference between the effects of the two materials.

The foregoing results explain in part why there are differences in the amounts of soil abraded by different drift materials. The drifted soils containing large amounts of sand or clay grains cause more abrasion than those containing loam aggregates (fig. 3), but the greatest factor is the proportion of fine dust contained in the blown material.

TABLE 2

Susceptibility of blocks of Haverhill loam to abrasion by various air-dry soil particles

SOIL MOISTURE AT PACKING	AMOUNT OF SOIL ABRADED BY 400 GM. OF								
	(a) Fine sandy loam containing much dust <0.05 mm.	(b) Mixture of sand and silt	(c) Clay containing much dust <0.05 mm.	Sand (0.42–0.83 mm.)	Clay (0.42–0.83 mm.)	Sand (0.25–0.42 mm.)	Clay (0.25–0.42 mm.)	Sand (0.1–0.25 mm.)	Clay (0.1–0.25 mm.)
per cent	gm.	gm.*	gm.*	gm.	gm.	gm.	gm.	gm.	gm.
17.6	13.1	+0.2	+2.9	42.0	39.9	36.1	32.6	33.6	21.6
22.2	0.2	+2.4	+4.4	9.1	9.8	8.4	7.8	9.4	4.6
26.9	0	+2.6	+4.4	5.4	4.8	5.7	3.4	6.7	1.8

Composition of abrasors (a), (b), and (c):

ABRASOR	SIZE DISTRIBUTION OF PARTICLES					
	>0.83 mm.	0.83–0.42 mm.	0.42–0.25 mm.	0.25–0.1 mm.	0.1–0.05 mm.	<0.05 mm.
	per cent	per cent	per cent	per cent	per cent	per cent
(a)	0	0	1.0	41.0	28.0	30.0
(b)	0	0	0	20.6	20.6	58.8
(c)	0	0	0	6.7	9.3	84.0

* Increase in weight due to adherence of fine dust to soil block.

Susceptibility of different degrees of roughness of surface to abrasive, detrusive, and extrusive action of wind-borne sand particles

Two degrees of roughness of surface were compared: the first, a surface with ridges 2.5 inches high and 9 inches wide, running at right-angles to the wind, and the second, a level surface, the projections of which did not exceed 0.5 inch in height. The soils were first exposed to wind for the length of time necessary for removal of all particles eroded off the surface by effluxion. Without change in the velocity of the wind, a stream of fine dune sand was then fed to the windward end of the soil area, which was 12 feet long and 20 inches wide. Figure 4 shows the net amount of soil deposited on or removed from a level surface throughout the course of exposure to the wind.

At the beginning of the exposure period under a 17-mile-per-hour wind at a 12-inch height, some abrasor was trapped in the slight irregularities of the

level surface of Sceptre heavy clay, thus causing an actual increase in the weight of the exposed soil (fig. 4).   The increase in the weight was virtually nil at the end of the first minute of exposure, but became very rapid thereafter and then diminished with continuation of exposure and finally reached 0 at the end of about 12 minutes.   At the end of the first minute a small quantity of abrasor was lodged between the surface obstructions, but this was counterbalanced almost equally by the weight of coarse clay granules which remained at rest under wind alone but which were removed by extrusion as soon as a sand stream was introduced.   Some of these granules were removed after the first minute of exposure, but the amount removed later was greatly exceeded by the weight of the incoming sand trapped between the irregularities of the exposed surface. At the end of 12 minutes these irregularities were smoothed out, and the amount of soil abraded by the incoming sand was too small to be detected.
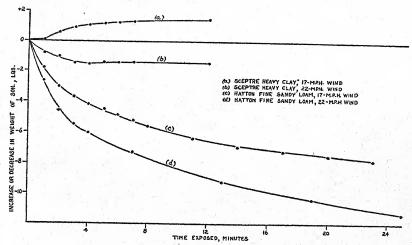
FIG. 4. SUSCEPTIBILITY OF A LEVEL SOIL SURFACE TO BOMBARDING ACTION OF DUNE SAND FED AT THE RATE OF 0.26 GM./CM. WIDTH/SECOND

Area of exposed soil 20 square feet

Somewhat different results were obtained with a 22-mile-per-hour wind. During the first minute of exposure there was a marked decrease in the weight of Sceptre heavy clay (fig. 4), showing that the amount removed under this velocity by extrusion was greater than the amount of sand trapped between the irregularities of the soil surface.   But subsequent exposure caused less and less difference between the weights of the deposited and removed material, until finally a constant weight of the exposed soil was maintained.   The continuation of the same weight under impacts of dune sand indicated this soil to be virtually nonabrasive, even under a high wind velocity.

The level surface of Hatton fine sandy loam, on the other hand, was markedly abraded by moving sand.   Despite trapping of sand between the irregularities of the surface, there was, under a 17-mile-per-hour wind, a marked net decrease in the weight of the exposed soil (fig. 4).   The decrease was at first relatively

great but diminished gradually until finally a constant rate of removal was reached. The high initial rate of erosion was due mainly to the removal of coarse granules initiated by impacts from a stream of sand, but after this loose material was removed, the subsequent rate of soil loss was dependent entirely on the rate of abrasion of soil lumps. The rate of abrasion was 0.1 and 0.15 pound per 2 pounds of sand abrasor blown by a 17- and a 22-mile-per-hour wind, respectively. This rate of abrasion, however, was not maintained but decreased gradually as a result of a change in soil texture, for, as a result of removal of fine fractions, more and more nonabrasive gravel and pebbles became exposed on the surface, thus covering and protecting the soil beneath. Had there been no gravel and pebbles, the abrasion rate would undoubtedly have remained the same.
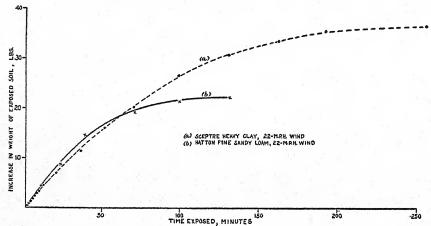
FIG. 5. SUSCEPTIBILITY OF A RIDGED SOIL SURFACE TO BOMBARDING ACTION OF DUNE SAND FED AT THE RATE OF 0.26 GM./CM. WIDTH/SECOND

Area of exposed soil 20 square feet

Figure 5 indicates the nature and the rate of deposition of dune sand blown over the ridged surfaces of two widely different soils. The rate of deposition on both soils was relatively rapid at first but diminished gradually and finally ceased. The constant weight of the exposed soil was obtained after the ridges disappeared. The disappearance of ridges was due to two factors: (a) the furrows being filled with the incoming sand, and (b) the ridges being worn down by the impacts of sand particles moving in saltation. The latter was manifested by three different forms of erosion: (a) complete removal of the semierosive grains by force of impacts of dune sand (extrusion); (b) disintegration of nonerosive clods that were exposed to the impacts of sand (abrasion); and (c) dislodgment of grains from the peaks of ridges with subsequent downward movement into the lee furrows (detrusion). The last form of erosion included the movement of the largest possible fractions that could be moved by the wind. Sceptre heavy clay was virtually nonabrasive, and the levelling process on this soil was due to the filling of the furrows with dune sand and to extrusion and

detrusion; but ridges over Hatton fine sandy loam wore down rapidly also, as a result of abrasion. Because of the relatively high susceptibility of this soil to abrasion the time required for complete smoothing of the ridged surface was only half that required for Sceptre heavy clay.

A total of 516 pounds of inflowing sand, or an equivalent rate of encroachment of 0.26 gram per centimeter width per second lasting for 4.3 hours, was required before a 12-foot long ridged surface of Sceptre heavy clay lost its trapping capacity completely. To produce this condition over a similarly ridged Hatton fine sandy loam, only 260 pounds were required. The ridged surface of Sceptre heavy clay was therefore about twice as effective in resisting the spread of soil drifting as that of Hatton fine sandy loam. The net amount of sand trapped by the ridges was 36 pounds on Sceptre heavy clay and only 22 pounds on Hatton fine sandy loam; the rest was blown past the exposed area. If there were no erosion of the soil at all, the ridges should have trapped all that the furrows could hold, that is, about 150 pounds of sand, instead of 35 and 22 pounds, respectively. It is evident, therefore, that both soils eroded badly, but whereas the manner of erosion of Sceptre heavy clay was mainly by extrusion and detrusion, that of Hatton fine sandy loam was also to a marked degree by abrasion.

DISCUSSION

The disintegration and movement of soil material by the wind is generally designated as *soil drifting* or *wind erosion*. Under either of these terms are included the translocating and the abrasive action of the wind. The terms *erosion, abrasion, corrasion,* and *deflation* have sometimes been used rather loosely in geological literature to denote specific forms of wind erosion. The terms *erosion, abrasion,* and *corrasion* have been used to designate detachment or loosening of soil particles from indurated materials, such as clods and surface crust, as a result of wear by impacts of soil or sand grains drifting along with the wind. In this paper, only the term *abrasion* is used in this sense, whereas the term *erosion* is given a much wider meaning to include any form of disintegration and movement of the soil material by the wind.

The term *deflation* has been used sometimes to denote the work of the wind in removing loose sand or soil particles (5), and sometimes to denote the blowing away only of fine dust, leaving loose erosive sand and coarser material behind (6). The former manifestation is not a result of any single form of erosion, but of several acting simultaneously. The latter, on the other hand, is a definite form of erosion. The term *deflation* is considered very inappropriate however, and the term *efflation* is used here to designate this form of erosion.

The results of experiments and general observation recorded in this and other papers of this series show that the wind acts on the soil in two general ways: by removing loose grains from the surface of the ground by direct pressure of its velocity, and by disintegrating and transporting the soil by force of impacts of the grains descending from saltation. Wind is much less erosive without particles of soil or sand drifting along with it, but is of great importance, nevertheless. The different forms of wind erosion found in this study are as follows:

1. *Effluxion*. This constitutes the removal of soil grains ranging from 0.1 to 0.5 mm. in diameter, initiated and maintained by the direct pressure of the wind. The removal is almost entirely by saltation, but a minor proportion of the soil may be removed in surface creep, and some fine particles may be picked up directly by the wind and carried away in true suspension.

2. *Extrusion*. This form of erosion occurs on soils that are composed of fractions too coarse to be removed by direct wind pressure. If, however, a field composed of these fractions is adjoined on the windward by an area containing particles removable by effluxion, many of these coarse fractions may be removed as a result of bombardment by the smaller grains. Extrusion is carried out chiefly by surface creep.

3. *Detrusion*. The peaks of surface projections are exposed to wind of a higher velocity than that over any part of a smooth surface. Consequently, if the surface was roughened, many of the coarser fractions not movable on a smooth surface would be readily dislodged from the crests of projections. Some of the finer grains would continue to bounce along the surface, but the coarser grains would be too heavy to pass through the zone of relatively low wind velocity between the projections (2) and would merely slide down into the lee depressions. The dislodgment of coarse soil grains from the tops of projections is particularly common on a ridged surface, especially under the bombarding action of highly erosive grains coming in from the windward side.

4. *Efflation*. Once lifted off the ground, fine dust particles, whose terminal velocity of fall in air is lower than the upward velocity of turbulent wind, are completely borne up by the wind. They usually reach great heights and do not fall to the ground except with the rain or after the wind has slackened considerably. Because of cohesion between these fine particles and the soil and because of the fact that the particles are generally too small to emerge above a laminar sublayer of air at the surface (3), they are seldom lifted directly by the wind, but mostly by impacts of larger grains moving in saltation. *Efflation*, as this form of erosion is called, is the removal of soil in suspension, resulting mainly from movement of coarser grains in saltation. It is most serious on arable soils because it constitutes a removal of fine soil constituents (chiefly silt and some clay), leaving the less mobile sand and gravel behind. As a result of this form of wind erosion, much of the arable soil in western Canada has become sandier than it was at the time of the breaking of the virgin sod (1).

5. *Abrasion*. Particles of dust and coarser fractions are being continually chipped off soil clods and other indurated materials as a result of impacts from grains moving in saltation. This form of erosion varies widely, depending on soil texture and other conditions, and is particularly prevalent on the leeward side of fields where the quantity of soil carried is the greatest. Abrasion is a direct result of movement in saltation.

This study has indicated that clay soils are most resistant to abrasion, but because of their high content of coarse granules they may be eroded by extrusion, that is, by removal of these grains as a result of bombardment by highly erosive particles coming in from a more highly erosive field on the windward. Loams and sandy loams, on the other hand, are readily abraded. A small quantity of sand particles originating from some spot in the field and passing over a sandy soil will often completely wear down the surface crust and cause the exposure of the highly erosive soil beneath. Calcareous clay soils seldom have a surface crust but may continue to resist the wind by virtue of their high content of coarse nonerosive or semierosive granules. Under the action of freezing and thawing, wetting and drying, as in the early spring, these coarse fractions may disintegrate to smaller, highly erosive particles. The soil will then drift, irrespective of whether or not there is an incoming flow of material. That is why drifting on calcareous clay soils is often more or less spontaneous over the entire

field, whereas over loams and sandy loams it usually starts from some highly erosive spot and extends fanwise to leeward as the surface crust protecting the soil is worn through by impacts of passing material.

The increased rate of erosion of the soil exposed to a bombarding action of highly erosive dune material is affected in three ways: first, by bombardment and resultant motion of the semierosive particles, which, under an equal wind velocity but without such bombardment, would remain at rest; second, by abrasion of the exposed nonerosive clods or surface crust; and third, in case of a rough surface, by detrusion of semierosive grains and resultant levelling of the surface.
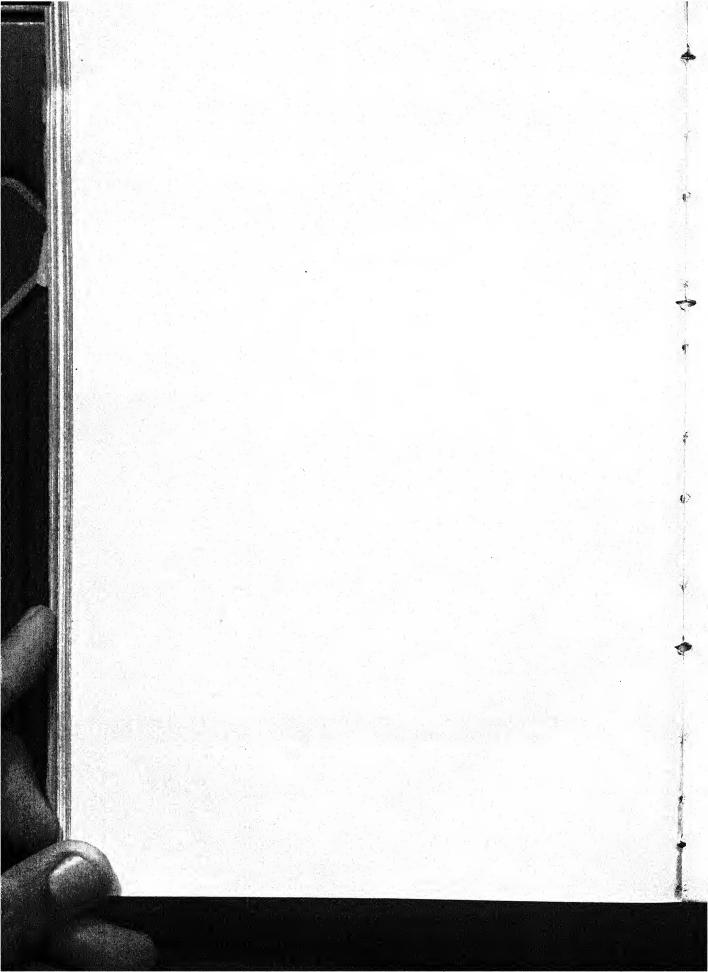
In conclusion, it may be said that erosion of the soil by effluxion is one of the most common forms of erosion. It is also the most important because all other forms are to a large extent a result of effluxion. This form of erosion is particularly serious on soils composed of the most highly erosive grains, which range from about 0.1 to 0.5 mm. in diameter. Hence, the whole program of prevention and control of wind erosion must be based on reducing the quantity of particles of this size, or else protecting the particles from the erosive action of the wind. Oftentimes a small highly erosive spot, from which soil particles may be removed by direct wind pressure, is sufficient to initiate erosion over an entire field. Such spots should be carefully watched and, if erosion is particularly serious, should be sown permanently to grass.

SUMMARY

It has been shown that arable soils are affected by five forms of wind erosion—effluxion, extrusion, detrusion, efflation, and abrasion. All, or some, of these forms may affect the soil simultaneously, but none of the other forms occurs on any appreciable scale without effluxion. Therefore, prevention and control of wind erosion should be based mainly on prevention of erosion by effluxion.

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RETENTION OF PHOSPHATES BY SOILS: IV. SOLUBILITY OF PHOSPHATES RETAINED BY VIRGIN HAMMOND VERY FINE SANDY LOAM TREATED WITH Ca(OH)$_2$ AND H$_3$PO$_4$[1]

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Considerable literature has been published on the subject of the fixation of phosphates by soils. The experimental data contained in different papers have been obtained under a wide variety of experimental conditions. The materials studied have included soils, soil colloids, claylike materials, and mineral colloids. Not only has there been a variation in the materials used, but the forms of phosphate and the associated cations and bases employed to vary the reaction have also varied from one experiment to another in many instances. The valid data obtained from most of the experiments have indicated results which sometimes do not appear to be in complete agreement with the results indicated by other equally valid data. Thus the question arises as to what effect some of these variable factors have upon the data obtained.

In a study of the factors affecting the retention of phosphates by soils, both phosphoric acid and monocalcium phosphate have been used to supply phosphorus. The data obtained with the same soil have had certain general similarities but differed markedly in others. Data on the effect of these forms of phosphate on the nature of phosphate retention as indicated by the cation-exchange capacity, exchangeable calcium, and soil reaction have been presented and discussed in previous papers (4, 5). Further data on the differential solubility of the phosphate when added as H$_3$PO$_4$ are given herein. Comparisons are also made of the solubilities of phosphorus obtained from samples of the same soil treated with H$_3$PO$_4$ and monocalcium phosphate

EXPERIMENTAL PROCEDURE AND METHODS

The Ca(OH)$_2$ and H$_3$PO$_4$ treatments used and the procedure followed for bringing the treated soil samples to equilibrium with the air have been described (5). The pH values of the suspensions were determined after 6-hour aspiration with air. The samples were then filtered, and the water-soluble phosphorus and calcium in the filtrate were determined. After the samples had dried and had been transferred to sample bottles, the dilute acid-soluble phosphorus was determined by Truog's method (10) and by a modification of the method (1).

After 6-year storage of the samples in the air-dry condition and at the time the reported studies (5) of the base-exchange properties were made, the following determinations of the solubility of the retained phosphate were made. Two-

gram samples of the soils were weighed into 500-ml. Squibb funnels containing 400 ml. of distilled H_2O. Water-washed CO_2 was bubbled through the suspensions for 1 hour. The reactions of the suspensions were determined with a Beckmann pH electrometer and the samples filtered. The pH values of the filtrates were also determined. The phosphorus in the CO_2-saturated water extracts was determined.

After the filtered samples had drained well, that is, for 5 to 6 hours, they were transferred on the filter papers to 750-ml. Erlenmeyer flasks, and 400 ml. of 0.002 N H_2SO_4 containing 3 gm. of $(NH_4)_2SO_4$ per liter of solution was added. They were tightly stoppered, shaken intermittently by hand for 30 minutes, and allowed to stand overnight. They were then filtered, and the pH values of the filtrate and the phosphorus dissolved in the dilute acid were determined. After being drained the samples were again placed in the original flasks and extracted with occasional shaking for 3 hours with 0.1 N H_2SO_4. The reaction and phosphorus content of the filtrates were determined.

EXPERIMENTAL RESULTS

The reactions of the soil suspensions after 6-hour aspiration with air have been given in the preceding paper (5). The phosphorus and calcium remaining in solution after equilibration with air are given in table 1. The phosphorus dissolved from the air-dried samples by 30-minute and 16-hour extraction with 0.002 N H_2SO_4 at pH 3.0 are also given in table 1.

H_2O-soluble phosphorus and calcium

The data in table 1 show that liming, in general, decreased H_2O-soluble phosphorus. The exceptions are plainly shown by the curves in figure 1, in which H_2O-soluble phosphorus is plotted as a function of the reaction at equilibrium. The curves show that maximum water solubility of phosphorus occurred at reactions of pH 5.0, 4.7 and 4.3 in the respective series to which 1.08, 2.16, and 4.32 millimols of H_3PO_4 per 100 gm. of soil were added. The decrease in H_2O-soluble phosphorus at reactions below these points is considered to be due to the precipitation of phosphorus as ferric phosphate.

A curve for the solubility of phosphorus obtained by titrating a series of samples of H_3PO_4 with $Ca(OH)_2$, carbonating with CO_2, and aspirating with air is shown in figure 1. The data were similar to those reported by Naftel (8). A comparison of this curve with the one obtained with soil shows the effect of the presence of soil on H_2O-soluble phosphorus. At reactions below pH 6.2, where the phosphorus occurred as H_3PO_4 and $Ca(H_2PO_4)_2 \cdot H_2O$, the soil markedly depressed H_2O-soluble phosphorus. At reactions above pH 6.2, the presence of the soil increased the H_2O-soluble phosphorus somewhat.

Water-soluble calcium increased with increasing amounts of lime added. The relatively large amounts of H_2O-soluble calcium obtained in the more acid samples of the series treated with 2.16 and 4.32 millimols of H_3PO_4 were associated with the large amounts of H_2O-soluble phosphorus in these samples.

TABLE 1

Water-soluble phosphorus and calcium after equilibration, and phosphorus dissolved by 0.002 N H_2SO_4 (Truog's reagent)
Treatment and results, per 100 gm soil

Ca(OH)₂ Added .... m.e. Sample Number	0 1	2.16 2	4.32 3	6.48 4	8.64 5	10.80 6	12.96 7	15.12 8	17.28 9	19.44 10
H_2O-soluble P—mmols.										
Ca(OH)₂ only—check	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
Check + 0.54 mmol. H_3PO_4	0.053	0.029	0.014	0.010	0.008	0.007	0.005	0.003	0.003	0.002
Check + 1.08 mmols. H_3PO_4	0.22	0.22	0.13	0.07	0.04	0.03	0.02	0.02	0.01	0.01
Check + 2.16 mmols. H_3PO_4	0.54	0.68	0.50	0.32	0.19	0.11	0.07	0.05	0.04	0.03
Check + 4.32 mmols. H_3PO_4	1.81	2.39	2.71	2.39	1.87	1.35	1.10	0.84	0.60	0.40
H_2O-soluble Ca—m.e.										
Ca(OH)₂ only—check	0.1	0.15	0.2	0.4	0.7	1.1	1.5	1.9	2.2	3.0
Check + 0.54 mmol. H_3PO_4	0.13	0.24	0.31	0.56	0.85	1.20	1.60	2.1	2.4	2.7
Check + 1.08 mmols. H_3PO_4	0.1	0.3	0.47	0.65	0.88	1.24	1.67	2.96	3.3	4.4
Check + 2.16 mmols. H_3PO_4	0.14	0.39	0.55	0.6	0.75	0.97	1.42	2.14	2.8	3.7
Check + 4.32 mmols. H_3PO_4	0.1	0.28	0.38	0.42	0.37	lost	lost	lost	lost	lost
P dissolved by 0.002 N H_2SO_4 in 30 minutes—mmols.										
Ca(OH)₂ only—check	0.013	0.014	0.014	0.014	0.014	0.015	0.015	0.015	0.015	0.016
Check + 0.54 mmol. H_3PO_4	0.21	0.25	0.27	0.28	0.29	0.30	0.32	0.33	0.34	0.34
Check + 1.08 mmols. H_3PO_4	0.39	0.44	0.56	0.63	0.69	0.72	0.76	0.77	0.79	0.81
Check + 2.16 mmols. H_3PO_4	0.75	0.75	0.93	1.18	1.35	1.53	1.63	1.69	1.72	1.75
Check + 4.32 mmols. H_3PO_4	1.16	0.96	0.87	1.23	1.75	2.32	2.62	2.94	3.22	3.44
P dissolved by 0.002 N H_2SO_4 in 16 hours—mmols.										
Ca(OH)₂ only—check	0.021	0.021	0.022	0.019	0.02	0.02	0.02	0.02	0.02	0.02
Check + 0.54 mmol. H_3PO_4	0.30	0.32	0.34	0.35	0.36	0.37	0.37	0.38	0.38	0.39
Check + 1.08 mmols. H_3PO_4	0.50	0.51	0.60	0.68	0.73	0.79	0.81	0.82	0.84	0.85
Check + 2.16 mmols. H_3PO_4	0.96	0.88	1.10	1.32	1.42	1.60	1.68	1.71	1.74	1.74
Check + 4.32 mmols. H_3PO_4	1.58	1.11	0.94	1.29	1.87	2.42	2.66	3.00	3.24	3.48

Retention of phosphorus

The relation of the phosphorus retained at the different levels of addition of
H_3PO_4 to the reaction of the soil samples after air-drying is shown in figure 2.
The curves for all levels of H_3PO_4 added show a minimum retention against
solution in water at a reaction of about pH 5.5.   It is of considerable interest
to note that this point of minimum retention occurs at the same pH in the air-
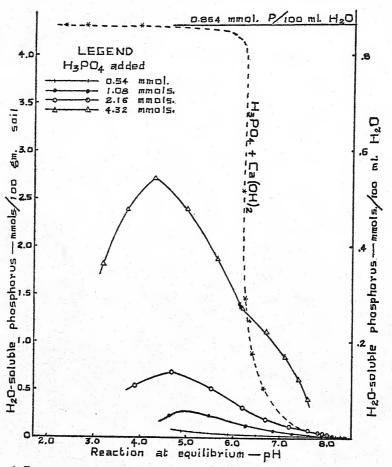
FIG. 1. RELATION OF H_2O SOLUBLE PHOSPHORUS TO REACTION OF SUSPENSION AT
EQUILIBRIUM

dry samples of all series, whereas in the original suspensions it occurred at pro-
gressively more acid reactions with increasing amounts of H_3PO_4 added.

The curves also show that the sorption capacity of the soil for phosphates
at pH 5.5 was nearly satisfied in the series to which 4.32 millimols of H_3PO_4 per
100 gm. of soil was added.   The amount retained was close to 1.57 millimols of
H_3PO_4, which on an equivalent basis was approximately 44 per cent of the
capacity of the soil to absorb calcium.

Possibly the most interesting point disclosed by these data is the difference in the behavior of the phosphate when added as H_3PO_4 and when added in the form of monocalcium phosphate. The derived data on the retention of phosphates when added in the form of monocalcium phosphate (2) and as H_3PO_4 are shown graphically in figure 3. The curves for the retention of H_2O-insoluble phosphorus and for phosphorus retained against solution in water and extraction for 30 minutes with 0.002 N H_2SO_4 are both shown. The curves show that at
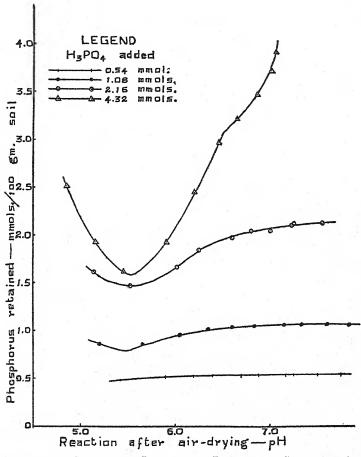
FIG. 2. RELATION OF PHOSPHATES RETAINED TO REACTION OF SOIL AFTER AIR-DRYING

reactions of pH 5.0 and of pH 8.0 and above, the amounts of H_2O-insoluble phosphorus for the H_3PO_4 and the $Ca(H_2PO_4)_2 \cdot H_2O$ series are very similar. At reactions between pH 5.0 and 8.0 the curves diverge—larger amounts of the phosphate were retained in the series to which H_3PO_4 was added. The amounts of phosphate removed by 0.002 N H_2SO_4 were similar for the two forms. Consequently the phosphorus retained against extraction with dilute sulfuric acid at soil reactions below pH 7.0 was somewhat more when added as H_3PO_4 than

it was when monocalcium phosphate was used. The more acid the reaction of the soil, the larger was the amount retained. The relatively close similarity of these curves for the two compounds of phosphorus contrasts sharply with the curves obtained by extraction of the soil with carbonated water.
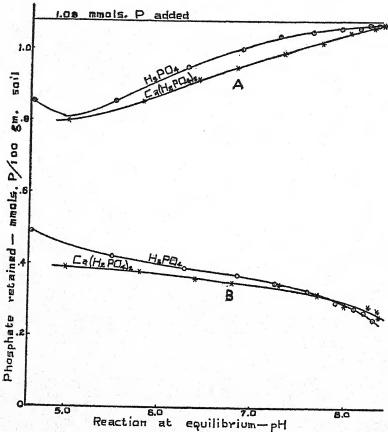
FIG. 3. PHOSPHORUS RETAINED: (A) INSOLUBLE IN WATER AND (B) INSOLUBLE IN H_2O PLUS 30 MINUTES' EXTRACTION WITH 0.002 N H_2SO_4

Phosphorus dissolved by CO_2-aspirated H_2O

The amounts of phosphorus dissolved by bubbling CO_2 through a suspension of 2.0 gm. soil in 400 ml. of distilled H_2O are given in table 2. The reactions of the CO_2-saturated suspensions before filtration and of the filtrates are shown in table 3. The data show that the amount of phosphorus soluble in carbonated water was increased by liming and by the addition of larger amounts of H_3PO_4. The increases obtained in the series to which 1.08, 2.16 and 4.32 millimols of H_3PO_4 were added were especially marked in the soil samples having reactions of pH 6.2 and above.

TABLE 2

Phosphorus dissolved by successive extraction in CO_2-saturated H_2O, 0.002 N H_2SO_4, and 0.1 N H_2SO_4 at reactions of pH 4.04–4.68, 3.12–3.20, and 1.35, respectively

Treatment and results, per 100 gm. soil

Ca(OH)₂ Added .... m.e. Sample number	0 1	2.16 2	4.32 3	6.48 4	8.64 5	10.80 6	12.96 7	15.12 8	17.28 9	19.44 10

P soluble in CO_2-saturated H_2O—mmols.

	0	2.16	4.32	6.48	8.64	10.80	12.96	15.12	17.28	19.44
Ca(OH)₂ + 0.54 mmol. H₃PO₄..............	0.03	0.04	0.05	0.06	0.07	0.08	0.10	0.10	0.11	0.13
Ca(OH)₂ + 1.08 mmols. H₃PO₄..............	0.09	0.07	0.08	0.22	0.35	0.41	0.46	0.56	0.58	0.58
Ca(OH)₂ + 2.16 mmols. H₃PO₄..............	0.19	0.22	0.34	0.53	0.84	0.98	1.23	1.35	1.45	1.45
Ca(OH)₂ + 4.32 mmols. H₃PO₄..............	0.27	0.30	0.36	0.58	1.01	1.45	1.80	2.24	2.71	3.09

P soluble in 0.002 N H_2SO_4—mmols.

	0	2.16	4.32	6.48	8.64	10.80	12.96	15.12	17.28	19.44
Ca(OH)₂ + 0.54 mmol. H₃PO₄..............	0.25	0.28	0.25	0.23	0.22	0.21	0.21	0.19	0.19	0.18
Ca(OH)₂ + 1.08 mmols. H₃PO₄..............	0.38	0.46	0.49	0.47	0.44	0.39	0.33	0.31	0.28	0.26
Ca(OH)₂ + 2.16 mmols. H₃PO₄..............	0.72	0.82	0.90	0.87	0.77	0.67	0.57	0.56	0.45	0.43
Ca(OH)₂ + 4.32 mmols. H₃PO₄..............	0.90	1.14	1.20	1.39	1.30	1.28	1.20	1.15	1.02	1.01

P soluble in 0.1 N H_2SO_4—mmols.

	0	2.16	4.32	6.48	8.64	10.80	12.96	15.12	17.28	19.44
Ca(OH)₂ + 0.54 mmol. H₃PO₄..............	0.15	0.14	0.15	0.15	0.14	0.13	0.13	0.13	0.13	0.12
Ca(OH)₂ + 1.08 mmols. H₃PO₄..............	0.33	0.30	0.30	0.28	0.27	0.26	0.23	0.22	0.21	0.21
Ca(OH)₂ + 2.16 mmols. H₃PO₄..............	0.64	0.48	0.41	0.38	0.36	0.34	0.28	0.26	0.26	0.25
Ca(OH)₂ + 4.32 mmols. H₃PO₄..............	1.16	0.78	0.58	0.56	0.56	0.45	0.42	0.41	0.41	0.40

TABLE 3

Reaction of extracting solutions

Treatment, per 100 gm. soil

Ca(OH)₂ Added.................................... m.e. Sample Number..	0 1	2.16 2	4.32 3	6.48 4	8.64 5	10.80 6	12.96 7	15.12 8	17.28 9	19.44 10

Reaction of CO_2-saturated H_2O suspension of soil—pH

	0	2.16	4.32	6.48	8.64	10.80	12.96	15.12	17.28	19.44
Ca(OH)₂ + 0.54 mmol. H₃PO₄..............	4.07	4.15	4.20	4.29	4.40	4.45	4.48	4.50	4.52	4.60
Ca(OH)₂ + 1.08 mmols. H₃PO₄..............	4.05	4.12	4.20	4.38	4.40	4.43	4.50	4.52	4.55	4.57
Ca(OH)₂ + 2.16 mmols. H₃PO₄..............	4.11	4.18	4.22	4.32	4.40	4.48	4.54	4.60	4.65	4.68
Ca(OH)₂ + 4.32 mmols. H₃PO₄..............	4.04	4.10	4.16	4.23	4.31	4.40	4.48	4.52	4.60	4.63

Reaction of CO_2-saturated H_2O filtrate—pH

	0	2.16	4.32	6.48	8.64	10.80	12.96	15.12	17.28	19.44
Ca(OH)₂ + 0.54 mmol. H₃PO₄..............	4.54	4.62	4.68	4.71	4.86	4.93	4.96	4.98	5.02	5.09
Ca(OH)₂ + 1.08 mmols. H₃PO₄..............	4.51	4.58	4.66	4.78	4.85	4.91	4.96	5.00	5.05	5.05
Ca(OH)₂ + 2.16 mmols. H₃PO₄..............	4.53	4.60	4.68	4.75	4.80	4.90	4.95	5.00	5.02	5.06
Ca(OH)₂ + 4.32 mmols. H₃PO₄..............	4.41	4.49	4.56	4.61	4.73	4.80	4.86	4.94	5.00	5.03

Reaction of 0.002 N H_2SO_4 filtered from soil—pH

	0	2.16	4.32	6.48	8.64	10.80	12.96	15.12	17.28	19.44
Ca(OH)₂ + 0.54 mmol. H₃PO₄..............	3.12	3.13	3.14	3.16	3.17	3.18	3.19	3.19	3.20	3.20
Ca(OH)₂ + 1.08 mmols. H₃PO₄..............	3.14	3.15	3.15	3.17	3.18	3.19	3.19	3.20	3.21	3.20
Ca(OH)₂ + 2.16 mmols. H₃PO₄..............	3.12	3.12	3.15	3.17	3.18	3.18	3.19	3.20	3.20	3.20
Ca(OH)₂ + 4.32 mmols. H₃PO₄..............	3.10	3.10	3.11	3.12	3.13	3.13	3.14	3.15	3.16	3.18

A comparison of the amounts of phosphorus dissolved in carbonated water from the series to which 1.08 millimols of phosphorus was added as monocalcium phosphate (3) and as H_3PO_4 is shown by the curves in figure 4. The addition of phosphorus as H_3PO_4 greatly decreased its solubility in carbonated water at
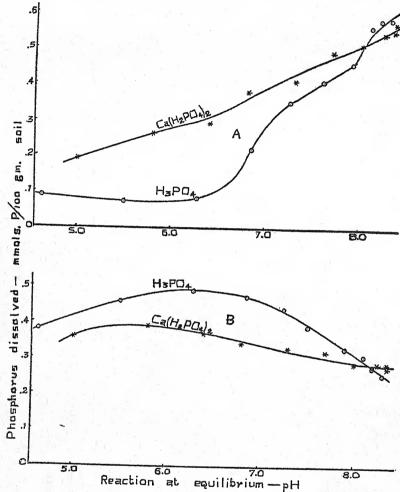
FIG. 4. PHOSPHORUS DISSOLVED (A) BY CARBONATED WATER AND (B) BY 0.002 N H_2SO_4 FROM SERIES TO WHICH 1.08 MMOLS PHOSPHORUS PER 100 GM. SOIL WAS ADDED

soil reactions below pH 6.4. The solubilities of phosphorus resulting from the use of the two forms were fairly comparable at soil reactions of pH 6.4 and above. The reactions obtained with the CO_2-saturated suspensions and filtrates from the samples treated with H_3PO_4 were practically identical with those for the samples treated with monocalcium phosphate (2).

Retention of phosphates against extraction in CO_2-saturated H_2O

The derived data for the phosphates retained against solubility in water and extraction with CO_2-saturated water are shown graphically in figure 5. There

were two minima of retention in each series.   The lowest retention was at the
most alkaline reactions, that is, between soil reactions of pH 7.0 and 8.0 in all
series.   The tricalcium phosphate or calcium carbonate-phosphate formed at
these reactions is insoluble in water but is brought into solution by CO_2.   Mc-
George and others (6, 7) have established the function of CO_2 in increasing the
solubility of phosphates in alkaline calcareous soils.   The other point of mini-
mum retention occurred in all series at a soil reaction near pH 5.5.   The increase
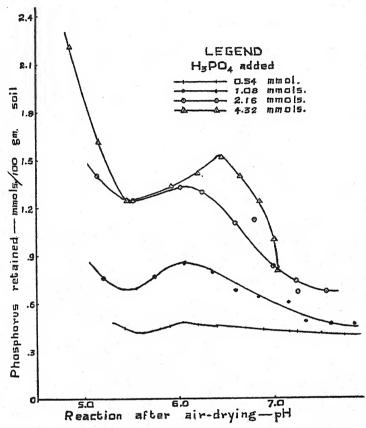
FIG. 5. PHOSPHATES RETAINED AGAINST SOLUBILITY IN WATER AND EXTRACTION WITH
CO_2 SATURATED WATER

in the retention of phosphates at reactions below pH 5.5 was very marked in
the series treated with the larger quantities, that is, 2.16 and 4.32 millimols of
H_3PO_4 per 100 gm. soil.   It is of interest to note the similarity of these data to
the data reported by Scarseth (9) on the retention of phosphates after carbona-
tion.   His data showed minima of retention at a reaction of pH 4.1.   The reac-
tions of the CO_2-saturated suspensions (table 3) of the samples in this work at
which these minimal retentions occurred were all between pH 4.07 and 4.18.
It would seem that the point at which this minimum occurs would be deter-

mined by the reaction of the soil at which fixation takes place rather than by the pH value of the extracting solution.

The retention of phosphorus when added as H_3PO_4 against solution in water and extraction with carbonated water differs considerably from that obtained when monocalcium phosphate was used (3). At soil reactions below pH 6.5 in the series treated with 1.08 millimols of P this retention in the H_3PO_4-treated series was from 20 to 40 per cent greater than it was in the series treated with monocalcium phosphate. Hence it seems that the form of phosphate used distinctly affects the manner in which it is fixed by the soil at acid reactions.

Phosphates soluble in dilute H_2SO_4

The amounts of phosphorus dissolved by the further successive extractions with 0.002 N H_2SO_4 and 0.1 N H_2SO_4 are given in table 2. The pH values of the soil-acid suspensions for the 0.002 N H_2SO_4 are given in table 3. These values varied from pH 3.1 to 3.2, being only very slightly less acid for the alkaline soil samples than for the acid soil samples. The reaction of all samples in 0.1 N H_2SO_4 suspensions was pH 1.35.

The amount of phosphorus dissolved by 0.002 N H_2SO_4 was largest in all series at reactions near pH 6.0. At both more acid and less acid soil reactions, it decreased. The amounts dissolved from the series to which 1.08 millimols phosphorus were added as H_3PO_4 and in the form of monocalcium phosphate (3) are shown in figure 4. At soil reactions between pH 5.2 and 7.0 more phosphate was dissolved by this extraction from the series to which H_3PO_4 was added. This shows that when H_3PO_4 is used the strength of retention is greater and indicates that the nature of retention may differ from that obtained with monocalcium phosphate.

The amount of phosphorus obtained in 0.1 N H_2SO_4, which was the last successive extraction, tended to increase with increasing soil acidity in all series. This was especially marked in the series to which 1.08, 2.16, and 4.32 millimols of phosphorus were added. In the series to which 1.08 millimols of H_3PO_4 was added the 0.1 N H_2SO_4-soluble phosphorus ranged from 0.33 to 0.21 millimols per 100 gm. soil, whereas in the series to which 1.08 millimols of phosphorus as monocalcium phosphate was added (3) the amount of phosphorus obtained by this extraction was practically a constant at 0.21 millimol regardless of soil reaction.

DISCUSSION

The differences in the solubility of the phosphate when added in the form of H_3PO_4 and when added as monocalcium phosphate (6) are of interest. Although the amounts of H_2O-soluble phosphorus obtained after the H_2O-Ca(OH)$_2$-soil-CO_2 systems had been brought into equilibrium with the CO_2 content of the air were relatively comparable for the two forms when added at the level of 1.08 millimols of phosphorus per 100 gm. soil, somewhat less phosphorus remained in solution, at all reactions, when it was added in the form of H_3PO_4 than when added as monocalcium phosphate. These values for the two forms of phosphorus were very similar at reactions of pH 5.0 to 5.5 and at reactions above pH 8.0 (fig. 3). They diverged at reactions between pH 5.5 and 8.0; those for

the H_3PO_4 series being smaller.   At soil reactions below pH 5.0 the H_2O-soluble phosphorus in the H_3PO_4-treated series decreased.

The amounts of phosphorus removed from the treated and air-dried samples by 30-minute extraction with 0.002 N H_2SO_4 (Truog's method) were also similar for the two forms.

The consecutive extractions of phosphorus made later with dilute acids (including carbonic acid) of successively greater strength showed some significant differences in the solubility of the phosphates retained by the soil from the two forms.   The last successive extraction made with 0.1 N H_2SO_4 at pH 1.35 brought virtually all of the added phosphate into solution, regardless of whether it was added as H_3PO_4 or as $Ca(H_2PO_4)_2 \cdot H_2O$ (3).   The actual amounts of phosphorus obtained by this extraction differed, however, for the two forms.   When added in the form of $Ca(H_2PO_4)_2 \cdot H_2O$, the amount obtained was virtually a constant at 0.21 millimol of P per 100 gm. soil regardless of soil reaction (3).   When added in the form of H_3PO_4, the amount obtained increased from 0.21 millimol P, for soil reactions of pH 7.6, to 0.33 millimol P, for soil reactions of pH 5.2.   The larger amounts obtained at the more acid soil reactions from the series treated with H_3PO_4 indicate a greater strength of retention of the phosphates by the soil.

In the consecutive extractions, more phosphorus was removed from the soil samples having a reaction below pH 8.0 by 0.002 N H_2SO_4 from the series treated with H_3PO_4 than from the series treated with monocalcium phosphate.

The most marked and probably the most significant difference in the solubility of the phosphate resulting from its addition as H_3PO_4 or as $Ca(H_2PO_4)_2 \cdot H_2O$ was that obtained with carbonated water extraction.   The amount of phosphorus soluble in CO_2-saturated water in the H_3PO_4-treated series was uniformly low at all soil reactions below pH 6.5.   This indicates that much of the phosphate retained by the soil at reactions below pH 6.5 is held differently when it is added in the form of H_3PO_4 than it is when added as monocalcium phosphate.   It is probable that extraction of the soil with carbonated water more nearly approaches the extracting power of growing plants for inorganic nutrients than does a pure water extract or an extraction with other dilute acids.   After making a study of the relation of soil pH to the solubility of phosphorus in water, carbonic acid, and 0.002 N H_2SO_4, Volk and Bell (11) noted, ". . . carbonic acid should be the most desirable solvent to use in estimating phosphorus availability in soils covering a wide range of pH."

Since the chemical form in which phosphates are added to the soil affects their subsequent solubility, it also affects the retention of the phosphate by the soil.   Thus the interpretation of data on the fixation of phosphates by soils should be made on the basis of the phosphatic compound used.   If fixation is interpreted as simply retention of phosphates against solubility in water, the differences obtained from H_3PO_4 and $Ca(HPO_4)_2 \cdot H_2O$ are not large.   On the other hand, when the weak acid, carbonated water, was used, marked differences were obtained.   Determinations of more than one level of solubility, such as H_2O-soluble phosphorus, are useful in understanding the manner of fixation of phosphates by soils.

SUMMARY

The solubility of phosphates in uniform series of samples of virgin Hammond very fine sandy loam treated with systematically varied amounts of $Ca(OH)_2$ and H_3PO_4, carbonated with CO_2, and brought to equilibrium with the CO_2-content of the air was studied. Data are given showing the effects of the treatments on H_2O-soluble phosphorus and the amounts of phosphorus removed from the soil by successive extractions with carbonic acid, $0.002\ N\ H_2SO_4$, and $0.1\ N\ H_2SO_4$ in relation to soil reaction. The differential solubility of the phosphorus resulting from treating the soil with H_3PO_4 is compared to that obtained, and previously reported, for similar soil samples treated with monocalcium phosphate. The data indicate that:

The amounts of soluble phosphorus obtained by successive extractions of the soil treated with 1.08 millimols H_3PO_4 per 100 gm. soil were significantly less than those obtained from the samples to which phosphorus was added in the form of monocalcium phosphate. The largest difference for the two forms was that obtained by extraction with carbonated water. At all soil reactions below pH 6.5, the amount of phosphorus soluble in CO_2-saturated water in the H_3PO_4-treated series was uniformly low; but at soil reactions above pH 7.0, it approached that obtained from the soil treated with monocalcium phosphate.

At soil reactions below pH 6.5 the phosphorus when added as H_3PO_4 became much less soluble in carbonic acid than when added in the form of monocalcium phosphate.

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BOOKS

Atomic Energy for Military Purposes. By HENRY D. SMYTH. Princeton University Press, Princeton, New Jersey, 1945. Pp. 264, plates 8. Price $2.

This is the full text of the official report on the development of the atomic bomb by the United States Government for military purposes. Included are four official photographs showing administration, production, and residential areas at Oak Ridge, Tennessee, and Pasco, Washington, and additional photographs of effects of the test in New Mexico. The author gives a brief review of the developments in nuclear physics between 1896 and 1940, and then tells the story of the scientific and technological teamwork that culminated in the making of the atomic bomb.

Brazil, Orchid of the Tropics. By MULFORD B. FOSTER AND RACINE SARASY FOSTER. The Jaques Cattell Press, Lancaster, Pennsylvania, 1945. Pp. 314, illus. 181. Price, $3.

This book takes you on a botanical trip through portions of Brazil, but not up the Amazon where most of the stories of the South American tropics begin. Each chapter deals with an interesting episode arising out of the day-by-day experiences of the authors as they go on their many expeditions to various parts of this immense country, which covers a larger land area than the United States of America. The illustrations are unique in that most of them present subjects that are new to the reader. One gets the impression that the book is the outgrowth not of a series of picnic trips but of many days of difficult and dangerous labor of the type that is more easily read about than done. As the statement on the cover indicates, no matter whether the reader is a traveler, a botanist, or an armchair adventurer, he will find beauty, danger, and practical fact of more than passing interest in this very attractive volume.

La Dynamique du Sol. Third Edition. By ALBERT DEMOLON. Dunod, Paris, 1944. Pp. 387, figs. 102.

The book is an outgrowth of a series of lectures that were first presented in 1930. It is divided into four parts, dealing with soil formation and the physical, chemical, and biological properties of soils, with an appendix on methods of soil analysis. All direct references are shown as footnotes at the bottoms of the pages and a list of supplementary-reading references is appended to each of the 17 chapters. The book is especially recommended to graduate students in soils who are in need of improving their reading knowledge of French. Some refreshingly new points of view are presented for their consideration.

Fluorochemistry. By JACK DE MENT. Chemical Publishing Co., Inc., Brooklyn, New York, 1945. Pp. 796, figs. 30. Price, $14.50.

This book has to do with the theory and application of fluorescence, luminescence, and other radiations. It also gives methods for the preparation of various luminescent dyestuffs and coloring matters and ultraviolet-emitting organic and

inorganic substances, with tests for their identification. The author quotes Henri Poincaré's "A collection of facts is no more a science than a heap of stones is a house," and then proceeds in an attempt to develop a concise science out of the known facts on fluorescence and related phenomena. The book is divided into five parts, at the end of each of which is a special bibliography, and contains five useful appendixes on nomenclature, atomic weights, the periodic system of the elements, energy data, and an abridged bibliography.

Photosynthesis and Related Processes. Volume I. Chemistry of photosynthesis, Chemosynthesis, and Related Processes in vitro and in vivo. By EUGENE I. RABINOWITCH. Interscience Publishers, Inc., New York, 1945. Pp. 599, figs. 63. Price, $7.50.

This is an exhaustive treatise on photosynthesis, its discovery, the chemistry of the process, and the structure and chemistry of the photosynthetic apparatus. The material is well organized, and the discussion deals with a great variety of subjects of interest to plant and soil scientists. An extensive bibliography, arranged chronologically, is appended to each chapter. The book should assume a highly important place in the literature of this fascinating subject and provide important reference material for all those concerned with the study of photosynthetic processes.

Rocks and Rivers of America. By ELLIS W. SHULER. The Jaques Cattell Press, Lancaster, Pennsylvania, 1945. Pp. 300, figs. 105. Price, $4.

This book is one of the "humanizing science series." The method of development of the subject is of the type employed in the demonstration-lecture, wherein interest is stimulated by presenting only the more spectacular features of each topic. In the absence of a classroom and demonstration table, and of the students in person, the author makes use of a much simplified approach and of a great many exceptionally fine illustrations. The soil conservationist will find the contents of the book quite in keeping with his own thinking and, for that reason, the volume is entitled to a place on the library shelf that is set aside for students in this field, as well as for those more intimately concerned with classical geology.

Wood Products for Fertilizer. Bulletin No. 7, Northeastern Wood Utilization Council, New Haven, Connecticut, 1945. Pp. 72. Price, $1.
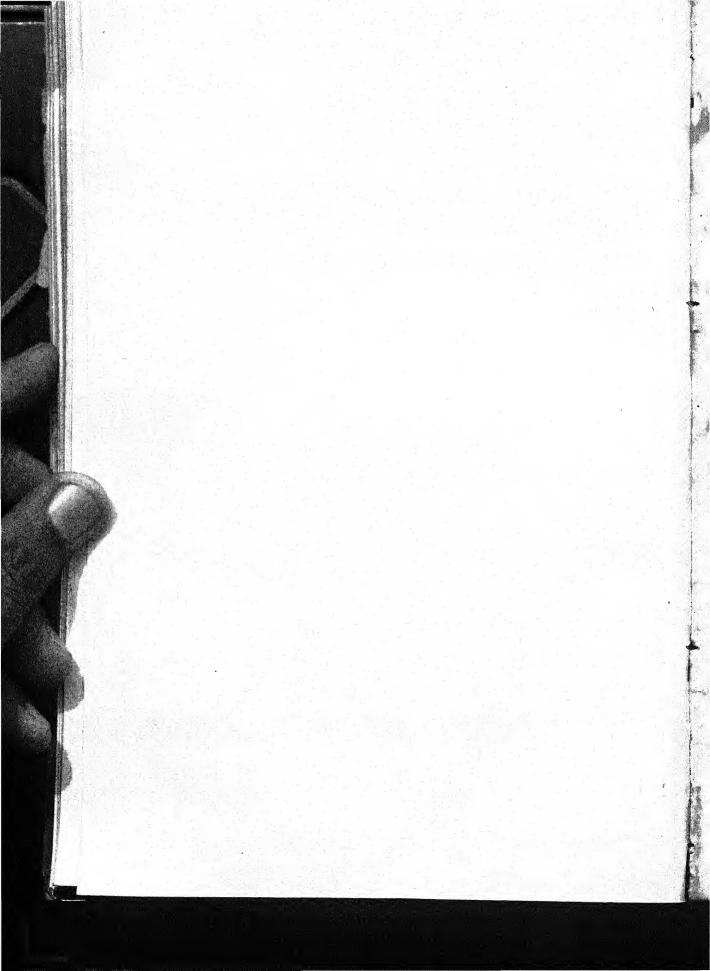
This is a report of a conference held at Orono, Maine, June 29, 1945, at which consideration was given to the possible usefulness of sawdust, shavings, and lignin as soil-improving agents. Papers were presented by J. A. Chucka, Herbert A. Lunt, Stuart Dunn, A. R. Midgley, J. W. White, Charles Thom, Joseph Seiberlich, and Robert S. Aries, and the report contains considerable supplemental discussion of the subject.

The World's Hunger. By FRANK A. PEARSON AND FLOYD A. HARPER. Cornell University Press, Ithaca, New York, 1945. Pp. 90. Price, $1.50.

The primary purpose of this very condensed presentation of the subject is to inform those who are concerned with the world food problem. The authors point out that there is a serious shortage of land with the proper combinations of topography, sunlight, temperature, rainfall, and fertility, and that under a "North American standard of living the present world production would maintain fewer than a billion persons, or less than half the present population." The several chapters deal with production, trade, consumption, moisture, temperature, land forms, soils, increasing production, food from water, and food and population problems. The authors suggest that Europe will be faced with the serious problem of adjustment either in her population or in her standard of living and that, as a result, she will continue to be a real danger spot to world peace. An important feature of this book is the appended bibliography.

THE EDITORS.

EFFECT OF MOISTURE CONTENT ON THE DISSOLVED AND EXCHANGEABLE IONS OF SOILS OF ARID REGIONS[1]

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The concentrations of the various ions in a soil solution generally do not vary inversely as the moisture content of the soil. The total dissolved quantities of some ions increase on dilution, while concurrently those of other ions may decrease. Changes in the relative and total concentrations of cations are simultaneously accompanied by shifts in the exchangeable-base status of the soil, because of the equilibriums existing between soluble and exchangeable cations. This latter principle applies also to the distribution of soluble and exchangeable anions. The complexity of these processes usually is intensified in soils of arid regions because of the greater abundance of soluble minerals and salts, the occurrence of slightly soluble salts such as gypsum and calcium carbonate, and the decreased solubility of some salts at high alkalinities. Knowledge concerning the nature and relative importance of the various processes occurring on dilution is applicable to the following fields of soil investigation: (*a*) methods of analysis of soluble salts; (*b*) methods of determination of exchangeable cations and anions; (*c*) variation of soil solution concentration and composition within the field range of moisture available to plants; (*d*) relation of physical properties to chemical composition; and (*e*) reclamation of alkali soils.

The present investigation was designed to re-examine the effects of dilution on the soluble and exchangeable ions of soils of arid regions and to interpret the findings according to our present knowledge of soil science.

REVIEW OF LITERATURE

The literature concerning the soluble salts of nonsaline soils has been reviewed at various times by Stewart (55), Parker (43), and Anderson, Keyes, and Cromer (2). Among the other investigations on nonsaline soils which are of interest in the present study are those of Martin *et al.* (8, 22, 35), Burgess (9), and Drachev and Alexandrova (15). The general method involved in these studies was the analysis of soil solutions[3] and extracts obtained from soil samples to which varying quantities of water had been added. Although universal agreement has not resulted from these investigations, several conclusions with respect to specific ions are generally accepted. The quantity of dissolved potassium usually increases with an increase in moisture percentage. Inceases in soluble calcium and magnesium often occur on dilution and result in changes in the calcium:magnesium ratio. The quantity of

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[3] In this paper, the term "soil solution" is applied to the solutions existing in or obtained from a soil at moisture contents within the field range.

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phosphate usually increases proportionally to the moisture content, which indicates that the solution is saturated with that ion. Total nitrate may increase or decrease slightly. Because of low concentrations of nitrate, some authors have ascribed small differences to experimental errors. Studies of sodium, sulfate, and chloride in nonsaline soils have been too few to warrant specific conclusions concerning their behavior. The usual net effect of increasing moisture is an increase in total dissolved salts. Several authors, however, have presented data indicating no changes in quantities of some ions and in total salts over wide moisture ranges, which indicates that various soils may react differently with water.

The effect of moisture content on the soluble salts of alkali, calcareous, and gypsiferous soils has been studied by Kelley and Brown (25), Hibbard (20), Menchikowsky and Ravikovitch (40), Eaton and Sokoloff (16), Kelley (27), Mulwani and Pollard (41), and Vanoni and Conrad (57). In virtually all cases, calcium, magnesium, sodium, potassium, carbonate, bicarbonate, sulfate, phosphate, and silicate increased on dilution. Several authors report approximately equal amounts of chloride and nitrate at different soil:water ratios. Eaton and Sokoloff (16), however, obtained significant decreases in dissolved chloride in three soils on increasing the moisture content from field moisture to 500 per cent. They explained this result by the postulate of "bound" water, in which salts would be insoluble or less soluble than in ordinary water.

Interrelationships among moisture content, dissolved cations and exchangeable cations have been studied by Kelley and Brown (26), Eaton and Sokoloff (16), Gardner, Whitney, and Kezer (19), Kelley (27), and Mulwani and Pollard (41). The replacement of exchangeable sodium by calcium derived from calcium carbonate by action of water and carbon dioxide was discussed at length by Kelley and Brown (26). This process appears to be important in the reclamation of some alkali soils. Eaton and Sokoloff (16) discovered that in three saline calcareous soils the dissolved calcium and magnesium decreased on dilution. Their explanation of this phenomenon lay in a cation exchange which ". . . takes place when the water:soil ratio is increased whereby calcium enters the absorbing complex and sodium is liberated." This process, which they called the "dilution effect," was obscured somewhat in their soils by the presence of calcium carbonate and gypsum. Subsequently, Kelley (27) presented data which indicate a decrease in dissolved calcium in one soil on dilution and possibly significant decreases in magnesium in two soils. Gardner, Whitney, and Kezer (19) showed that some slick-spot soils which contain high proportions of exchangeable sodium at field moisture tend to become saturated with calcium and magnesium on washing with distilled water. Mulwani and Pollard (41) conclude that soluble and exchangeable base values of saline and alkaline soils obtained by means of water extracts are applicable only at the moisture content of the extract.

Unfortunately, many of the results of previous workers were influenced by experimental variables other than simple dilution, *per se*. Anderson, Keyes, and Cromer (2) stress the importance not only of soil:water ratio but of time and microbiological activities on the composition of the soil sultion. Several workers have employed techniques which tended to avoid effects of time and biological processes, but others have ignored them, while some have not been sufficiently explicit in their descriptions of procedure. In a recent paper by Magistad, Reitemeier, and Wilcox (33), soluble salt information on four soils at moisture contents from field range to 500 per cent was presented. All the moist soil samples involved in that study stood for 2 weeks before filtration, and it is now recognized that some of the results were affected by the unequal influence of microbiological activities at different moisture contents.

PLAN OF INVESTIGATION

The present investigation was based on the theory that there is only one acceptable procedure for studying the effect of simple dilution on soluble and exchangeable ions. This comprises (*a*) the preparation of a soil sample at field moisture, (*b*) providing sufficient time and mixing for moisture equalization, (*c*)

addition of calculated quantities of water to subsamples followed by satisfactory agitation, (d) extraction of all the solutions immediately after adequate equilibration of the subsamples with the added water, and (e) prompt analysis of the solutions.

In carrying out this procedure, six air-dry soil samples which had been passed through a ⅛-inch sieve were sprinkled with sufficient boiled distilled water to increase the moisture content to a value between the wilting range and the moisture equivalent. The moistened samples in friction-top tinned cans were kept in a constant temperature room at $21 \pm 0.5°$ C. for 2 weeks, during which period they were removed from the cans at intervals of 3 or 4 days and mixed by rolling on a Koroseal mixing cloth. Immediately following the last mixing, part of each sample was placed in a pressure-membrane apparatus (48, 49), and the extraction of the soil solution commenced under an air pressure of 220 pounds per square inch. On the next day, three soil suspensions, containing the saturation percentage (33, 54), 200 per cent (1:2 suspension), and 500 per cent (1:5 suspension) of water were prepared from the remainder of the moist sample by the addition of the proper quantities of boiled distilled water. The saturation suspensions were mixed by stirring and the more dilute samples by shaking 1 hour on a reciprocating shaker. All suspensions were filtered on the same day through "ashless" filter paper in Büchner funnels by means of vacuum furnished by a water aspirator. The soil solutions and extracts were removed in fractions, each portion was treated with 2 p.p.m. of sodium hexametaphosphate to prevent precipitation of calcium carbonate on standing (47), and fractions were composited on the basis of electrical conductivity measurements. Analyses were started immediately and the ions determined in the following order: NO_3, NH_4, CO_3, HCO_3, Cl, Ca, Mg, Na, K, SO_4, PO_4. Most of the analyses involved two or three fractions of each solution. In a previous paper (48), it was shown that the calcium, magnesium, or bicarbonate concentrations of pressure-membrane solutions from calcareous soils sometimes increase during the extraction because of the microbiological production of carbon dioxide. This process affected these three ions in soils 85 and 183, and the bicarbonate of soils 58 and 86. The initial values for the concentrations of the affected ions were selected because it was thought they were more representative of the conditions affecting the preparation of the more dilute suspensions.

The pH values of the 24 soil samples and the composited solutions were measured with a glass electrode assembly. In addition, that of the field moisture samples diluted to the sticky point was measured. Because the values for the extracts were erratic, evidently a result of the vacuum and contact with glass, pH was redetermined on fresh suspensions and on the extracts obtained from them by centrifuging.

Base-exchange capacity and the quantities of calcium, magnesium, sodium, and potassium extractable by ammonium acetate were determined on the field moisture samples. Extractable ammonium[4] was determined on one soil.

[4] "Extractable" as used in this paper includes the exchangeable, soluble, "fixed," and other sources of cations which are extracted from a soil by the particular ion replacement technique employed.

MATERIALS AND METHODS

The six soil samples were from locations in four Western States. The Palouse loam sample, no. 65, originally a leached acid soil having a pH value of 5.5 at saturation percentage, was treated with NaOH and NaCl to provide a noncalcareous, neutral, saline soil for further investigation of the "dilution" effect found by Eaton and Sokoloff (16) in calcareous soils. Pertinent information concerning the soils is presented in table 1.

None of the samples contained an extremely high salt content such as is sometimes encountered. The percentages shown were calculated from the analyses of the soil solutions obtained at field moisture. All salt and moisture percentages

TABLE 1
Some characteristics of soil samples

ACCESSION NUMBER	SOIL TYPE	LOCATION	DEPTH	SOLUBLE SALTS	CaCO₃ *	GYPSUM	ORGANIC C	MOISTURE RETAINED AT			EXTRACTION MOISTURE		
								15 atm.	$\frac{1}{3}$ atm.	$\frac{1}{10}$ atm.	Pressure membrane		Saturation
			in.	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*atm.* †	*per cent*
56	Imperial clay loam	Meloland, Calif.	6–18	0.14	13.1	0.1	0.34	15.1	27.2	29.7	20.5	3	63.7
58	Indio very fine sandy loam	Coachella, Calif.	6–18	0.08	4.7	0	0.20	6.1	18.4	21.6	15.2	1	41.4
65	Palouse loam	Pullman, Wash.	2–6	0.34	0	0	1.50	10.6	20.8	23.7	18.4	1	44.9
85	Reagan loam	Roswell, N. Mex.	2–8	0.17	13.0	3.0	0.93	11.4	19.8	23.2	17.5	1	40.7
86	Fort Collins loam, poorly drained phase	Laramie, Wyo.	1–6	0.46	3.3	4.8	0.99	11.8	19.5	22.4	19.6	0.5	45.6
183	Hesperia sandy loam	Shafter, Calif.	0–8	0.03	0.1	0	0.48	4.7		10.6	9.5	0.5	28.4

* Includes MgCO₃ if present.
† Approximate tension by interpolation.

are based on soil oven-dried at 105° C. The CaCO₃ contents were determined by addition of an excess of N HCl and back-titration with N NaOH to the pH which the soil would have at the soil:water ratio involved. The gypsum ($CaSO_4 \cdot 2H_2O$) contents of soils 85 and 86 were determined by successive water extractions and centrifugations, followed by conductivity measurements on each extract, and by determination of calcium and sulfate on the composited extracts; the two methods agreed surprisingly well. The organic carbon contents were determined by a method involving the chromic acid procedure of Schollenberger (53) and the modified phosphoric acid reagent of Purvis and Higson (45).

The 15-atmosphere moisture percentage usually lies in the wilting range between the "first permanent wilting percentage" and the "ultimate wilting per-

centage" (51) and somewhat below the "permanent wilting percentage" (50). The moisture equivalent of coarse- and medium-textured soils approximates the $\frac{1}{3}$-atmosphere percentage (51), whereas in fine-textured soils it tends to approach the $\frac{1}{2}$-atmosphere percentage (50). The moisture percentages of the gypsiferous soils have not been corrected for the loss of water of crystallization from gypsum during oven-drying.

Most of the analytical determinations on the soil solutions and extracts were made by semimicroanalytical methods outlined elsewhere (46). Other methods used have been described by Magistad, Reitemeier, and Wilcox (33). Calcium and magnesium in the solutions from soil 86 were determined after reprecipitation of the calcium as oxalate. Because of its low concentration, chloride in the solutions from soil 183 at the three highest moisture contents was determined by titration with mercuric nitrate using diphenylcarbazone as indicator (52). The sulfate contents of the same solutions are not reported because they were so low that accurate values were not attainable. Separate values for carbonate and bicarbonate are not reported because titration methods cannot distinguish precisely between the two ions (21). Kelley and Brown (25) previously regarded the value of the usual distinction between carbonate and bicarbonate as questionable. The concentration reported here is essentially the alkalinity to methyl orange. Lack of sample precluded phosphate determinations on the soil solutions.

The ion concentrations are expressed on the oven-dry soil basis, in units of equivalents per million (e.p.m.). An equivalent per million is one unit chemical equivalent weight per million unit weights of soil or of solution. On the soil basis 1 e.p.m. is identical to 1 m.e. per kilogram of soil, and on the solution basis (specific gravity of unity) to 1 m.e. per liter of solution. The unit was adopted by the American Society of Testing Materials (1, p. 541) and is discussed in detail elsewhere (33). To convert the reported values on the soil basis to the solution basis, the following formula should be used:

$$\text{E.p.m.}_{\text{solution}} = \frac{100 \times \text{e.p.m.}_{\text{soil}}}{\text{per cent water}} \qquad (1)$$

The bases extractable by ammonium acetate were determined by a procedure involving successive extractions by neutral normal ammonium acetate, agitation, and centrifugation. It is planned to publish the details of this method later. Bower and Truog (4) employed a method based on the same general principles. After the same samples had been washed with ethanol, the adsorbed ammonia (base-exchange capacity) was determined by replacement with potassium and straight nesslerization of an aliquot of the potassium chloride extract.

Because Chapman and Kelley (10) found the adsorbed ammonia of the soil they studied to be reduced 10 per cent by adsorption of calcium dissolved from calcium carbonate, and Reitemeier and Fireman have obtained an average reduction of 11 per cent in five soils, the samples of soils 56, 58, 85, and 86 were extracted with ammonium acetate until all the carbonates had been removed. Extractable ammonium in Palouse loam was determined in a fresh sample by replacement with calcium, followed by distillation and nesslerization.

The total soluble bases at each moisture content were subtracted from the total extractable bases. On all soils except Palouse loam, the corrected values were higher than the capacities. This results from the extraction by ammonium acetate of bases other than those water-soluble and truly exchangeable, from such sources as calcium and magnesium carbonates, gypsum, "fixed" potassium and other bases, silicates, and other soil minerals. Because of this, the directly determined exchangeable values were used only for sodium, and those for Ca, Mg, and K were calculated from the concentrations of soluble bases and quantitative information concerning equilibria between the various soluble and exchangeable bases. Some recent studies of Reitemeier and Fireman indicate an average replacing ability ratio of K to Na of 5. The exchangeable K values have been calculated from the following equation, based on this ratio:

$$KX = 5 \cdot NaX \cdot \frac{(K^+)}{(Na^+)} \tag{2}$$

where KX and NaX are the quantities of exchangeable K and Na, respectively, in milliequivalents per 100 gm. of oven-dry soil, and (K^+) and (Na^+) are the soluble concentrations of K and Na. This formula was not used for the exchangeable K of soil 85, for which subtraction of the soluble K from extracted K provided more consistent values.

Similar equilibrium studies with calcium and magnesium indicate a replacing ability ratio of calcium to magnesium of 1.6. This agrees well with the average value of 1.5 obtained by Kerr (28, 29) on three inorganic soils, and an average "relative ease of release" ratio of 1.56 found by Bray (5) on seven soils. The exchangeable calcium and magnesium of all soils except Palouse loam have been calculated on the basis of this ratio by means of the following equations, in which CaX and MgX signify the exchangeable Ca and Mg in milliequivalents per 100 gm. of soil, and DX equals the sum of CaX and MgX:

$$\frac{(Mg^{++})\, CaX}{(Ca^{++})\, MgX} = 1.6 \tag{3}$$

$$CaX + MgX = \text{B.E.C.} - NaX - KX = DX \tag{4}$$

$$MgX = DX\, \frac{(Mg^{++})}{(Mg^{++}) + 1.6\,(Ca^{++})} \tag{5}$$

$$CaX = DX - MgX \tag{6}$$

EXPERIMENTAL RESULTS

pH values

The pH values are listed in table 2. Two general relationships are apparent, namely: (a) close agreement between the pH of the suspension and that of the solution, especially for the centrifuged samples, and (b) an increase in pH with increasing moisture content. The centrifugation technique probably causes less change in pH value of an extract than does the soil solution extraction procedure.

McGeorge (31) obtained similar order of agreement on 1:1 suspensions and their centrifuged extracts. It can be concluded that the pH values of these soil samples are substantially identical with those of their solution phases. It is recognized that pH measurements with glass electrodes on soils below the moisture equivalent have been criticized by Davis (14). Appreciable time was required for the pH values of the field moisture samples to become "constant."

The increase in pH on dilution is well known (11, 31). Whitney and Gardner (59) concluded that this effect is probably due primarily to reduction of carbon dioxide concentration on dilution. The pH values of the two gypsiferous soils, 85 and 86, increased but slightly on dilution, because of the repression of clay mineral hydrolysis by the calcium sulfate dissolved by additional increments of

<div align="center">

TABLE 2

pH values of soil suspensions and solutions

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ACCESSION NUMBER	SYSTEM	pH VALUES AT VARIOUS MOISTURE CONTENTS				
		Field moisture	Sticky point	Saturation percentage	200 per cent	500 per cent
56	Suspension	7.45	7.65	7.83	8.27	8.68
56	Solution	7.32	....	7.91	8.13	8.48
58	Suspension	8.32	8.63	8.83	9.72	10.05
58	Solution	8.46	....	8.72	9.64	9.99
65	Suspension	6.73	6.85	6.90	7.37	7.68
65	Solution	7.36	....	7.41	7.28	7.63
85	Suspension	7.55	7.73	7.65	7.83	8.01
85	Solution	7.85	....	7.64	7.82	7.92
86	Suspension	7.70	7.76	7.87	7.94	8.06
86	Solution	7.92	....	7.94	7.87	7.98
183	Suspension	7.39	7.57	7.73	8.50	8.77
183	Solution	7.74	....	....	....	8.61

water. McGeorge (31) found that increasing concentrations of either calcium or sulfate ions result in decreased pH values. The pH of sample 58, a "black alkali" soil, increased to 10 on dilution to 500 per cent of water.

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Dissolved ions

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The variation with moisture content of soluble ions in the six soil samples is shown in figures 1 to 6, inclusive. The curves for each soil except Hesperia sandy loam are drawn to two scales because of the extreme range among concentrations of the various ions. The individual ions are discussed in the order in which they are usually reported.

Calcium. In soils 85 and 86 total dissolved calcium increased by 17- and 33-fold on dilution because of the continuous solution of excess gypsum. In soil 86
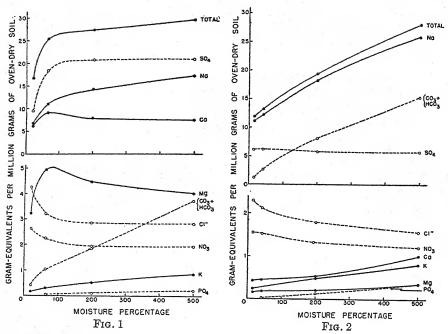
FIG. 1. EFFECT OF MOISTURE CONTENT ON DISSOLVED IONS OF IMPERIAL CLAY LOAM
(SOIL 56)

FIG. 2. EFFECT OF MOISTURE CONTENT ON DISSOLVED IONS OF INDIO VERY FINE SANDY
LOAM (SOIL 58)
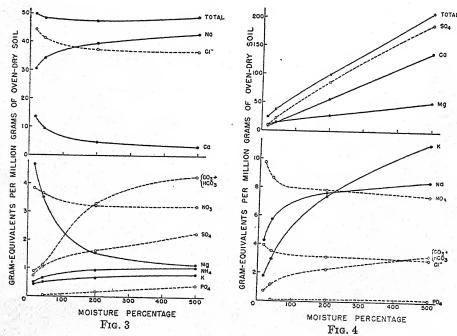
FIG. 3. EFFECT OF MOISTURE CONTENT ON DISSOLVED IONS OF PALOUSE LOAM (SOIL 65)
FIG. 4. EFFECT OF MOISTURE CONTENT ON DISSOLVED IONS OF REAGAN LOAM (SOIL 85)

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the solution concentration of Ca remained virtually constant with increasing moisture because of a considerable quantity of Na_2SO_4 and $MgSO_4$. Vanoni and Conrad (57) present results of a similar nature on a gypsiferous soil in which the sulfate concentration in the solution remained constant because of the presence of $CaCl_2$. In soil 183, calcium increased slightly on dilution. This increase was due mainly to solution of $CaCO_3$, and its extent was reduced by exchange of some of the calcium thus dissolved for sodium and potassium. On longer standing, the soluble calcium in the dilute suspensions of this soil increased to much higher values because of the microbiological formation of carbon dioxide [see Magistad,
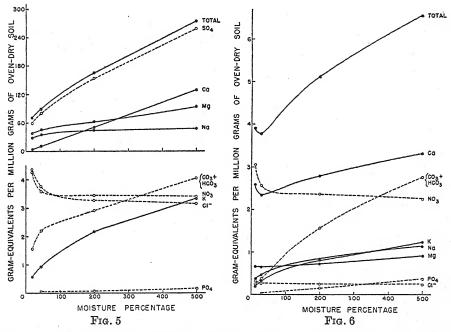
FIG. 5. EFFECT OF MOISTURE CONTENT ON DISSOLVED IONS OF FORT COLLINS LOAM (SOIL 86)
FIG. 6. EFFECT OF MOISTURE CONTENT ON DISSOLVED IONS OF HESPERIA SANDY LOAM (SOIL 183)

Reitemeier, and Wilcox (33)]. The minimum value occurring at the saturation percentage is attributed to the method of extraction; some carbon dioxide was probably removed during the vacuum filtration of the three dilute suspensions with consequent precipitation of $CaCO_3$. In soil 58, the Ca was approximately doubled on dilution but remained at a low level because of the relatively high pH and carbonate content. Because of the relatively great ability of Ca to replace exchangeable sodium, however, extensive transfer of calcium from the carbonate to the solution and thence to the exchange complex occurred on dilution. In soil 56, the dissolving of gypsum caused an increase to the saturation percentage, followed by a decrease. This latter is an example of the "dilution" effect of Eaton and Sokoloff, and it is of interest that soluble calcium can pass through a

maximum value under the conditions occurring in this soil. Soil 65, which was selected and treated in order to study the "dilution" effect, showed the effect distinctly. The soluble calcium decreased from 13.5 to 3.1 e.p.m. on dilution, and this was accompanied by a decrease in magnesium and by increases in the monovalent ions sodium, potassium, and ammonium.

Magnesium. In these soils, the soluble magnesium was affected by moisture content similarly to calcium except that the effect occurred at lower levels. In soil 56, the ratio between the 500 per cent extract and the soil solution was 1.24, and for calcium it was 1.23; for soil 65, the two ratios were 0.246 and 0.230, respectively. In calcareous soils it is difficult to distinguish between the magnesium rendered soluble by solution of magnesium carbonate and that replaced from the exchange complex by calcium. In soils 85 and 86, the calcium:magnesium ratio increased considerably on dilution, from 0.87 to 2.70 and from 0.10 to 1.34, respectively.

Sodium. All six soils demonstrated increased soluble sodium on dilution. The main source of this is adjudged to be replaceable sodium of the exchange complex, although there is evidence that slightly soluble sodium minerals might have been involved. Because of its low relative replacing ability, exchangeable sodium is replaced by calcium, magnesium, potassium, and possibly other ions, originating from soluble salts, gypsum, calcium and magnesium carbonates, silicates, aluminosilicates, phosphates, and other soil minerals. The increase of sodium in soil 65 is attributed to the cation "dilution" effect, that is, on simple dilution, soluble calcium and magnesium replaced exchangeable sodium from the colloids, which then appeared as soluble sodium. In soil 56, a portion of the increased sodium appearing between saturation percentage and 500 per cent moisture is likewise associated with the decrease in calcium and magnesium throughout this moisture range. The extent of replacement of sodium (and other cations) by hydrogen on dilution of the soil salts varies with the soil conditions. This hydrolysis probably was slight in soils 56, 65, 85, and 86 because of their relatively high contents of neutral salts. The greater increase in pH of soils 58 and 183 on dilution, however, is evidence of appreciable hydrolysis. The increase in soluble sodium in these two soils probably resulted from exchange of hydrogen from water and of calcium from $CaCO_3$ (6, 26).

Potassium. On dilution, potassium increased in all soils in amounts varying from 90 to 540 per cent. Because of the low potassium level, however, this did not alter the cation ratio appreciably in soils 56 and 86. The increase in potassium appears to be characteristic of both humid and arid soils. The distribution of potassium among solution, exchange complex, and minerals is influenced by the same factors affecting sodium. Additionally, the extent of solution of "fixed" potassium by water and salt solutions may be important and is difficult to estimate (44). A large fraction of the increase in soils 85 and 86 probably resulted from the solvent action of gypsum solutions on this source of potassium.

Ammonium. Only soil 65 contained an appreciable quantity of ammonia, presumably because it was acidic. The soluble ammonia doubled on dilution, because of replacement from the exchange complex by calcium and magnesium.

The percentage increase was almost identical with that of potassium, which leads to the conclusion that the increase in both these ions in this soil was due solely to the divalent-monovalent cation dilution effect.

Carbonate-bicarbonate (alkalinity).   These two ions and other titratable anions have been grouped under the term "alkalinity" for convenience in this discussion. The alkalinity of all six soils increased with moisture content, and the order of percentage increase agreed exactly with the order of rise in pH.   The ratios of alkalinity at 500 per cent moisture to that at field moisture for the six soils were, respectively, 9.2, 13.5, 4.8, 4.8, 2.6, and 12.0.   These tremendous increases were not the result of prolonged time of contact of soil with water, as the diluted suspensions were filtered shortly after preparation.   All soils except 65 were calcareous, and their increased alkalinity is attributed to carbonates dissolved by the additional water and to chemical reactions which occurred on dilution.   Such reactions were most pronounced in soil 58, because of the hydrolysis of the sodium clay accompanied by the solution of calcium carbonate to maintain exchange equilibrium.   For this soil, the sodium and alkalinity curves are virtually parallel because each sodium ion displaced from the colloid was balanced by a carbonate or bicarbonate ion derived from $CaCO_3$.

The increase shown by soil 65 cannot be explained on the basis of solid-phase carbonate, because this soil had a pH value of 5.5 prior to treatment with sodium. The increase is attributed to anion exchange between bicarbonate and hydroxyl ions.   The work of Mattson (36) has demonstrated the adsorption of chloride, sulfate, and phosphate ions over varying pH ranges and the extremely high effectiveness of hydroxyl ions in replacing them, especially chloride ions.   No similar report on bicarbonate adsorption and replacement has been seen.   It is postulated that the increase in hydroxyl ion activity (rise in pH) on dilution results in replacement of adsorbed bicarbonate ions.   This idea is supported by the shape of the alkalinity curve, in that the slope is appreciably reduced at the higher dilutions, which accords with Mattson's conclusion that monovalent ions are adsorbed appreciably only in acid solutions.

Sulfate.   In soils 56, 85, and 86, sulfate increased on dilution because of the continuous solution of additional increments of gypsum.   In soil 56, this occurred until its small quantity of gypsum was completely dissolved, at a moisture content of about 100 per cent, above which sulfate remained constant.   Soil 58 showed a virtually constant amount, about 6 e.p.m., throughout the entire moisture range.   In soil 65, sulfate increased from 0.73 to 2.25 e.p.m., which is explained as an anion replacement by hydroxyl ions.   Mattson (36) found sulfate adsorption to decrease with increase in pH.   Mattson and Wiklander (39) mentioned a Puerto Rico soil the sulfate of which was completely dialyzable only after the soil was made alkaline with ammonia.   Eaton and Sokoloff (16) and Kelley (27) have suggested that sulfate adsorption may explain increases on dilution of some soils.   Coles and Morison (12) extracted 0.18, 0.23, 1.37, and 3.62 per cent of sulfate from four acid soils by repeated heatings and water extractions.

Chloride and nitrate.   Chloride and nitrate are discussed together because the two ions acted alike in all six soils.   Decreases in both ions occurred throughout

the entire moisture series, the rate of reduction being higher in the low moisture range. Within the field moisture range of some soils the content dropped abruptly. The percentage reduction at the various dilutions is shown in table 3. With due consideration for the wide diversity in soils and the differences in relative wetness among the field moisture samples, the agreement of reductions in soluble chloride and nitrate in all soils between field moisture and 500 per cent water is regarded as excellent. It suggests that only one mechanism was involved in the decreases. The mean chloride and nitrate reductions were 28 and 23 per cent, respectively. Decreases in chloride on dilution are contained in the results of Eaton and Sokoloff (16) and Kelley (27). Reductions in nitrate in some soils are shown by the results of Parker (43), Burgess (9), and Burd and Martin (8).

TABLE 3

Percentage reduction in soluble chloride and nitrate on dilution

ACCESSION NUMBER	ION	PERCENTAGE REDUCTION AT VARIOUS MOISTURE CONTENTS			
		Field Moisture	Saturation Percentage	200 per cent	500 per cent
56	Chloride	0	24	33	34
56	Nitrate	0	15	27	27
58	Chloride	0	7	22	32
58	Nitrate	0	1	14	22
65	Chloride	0	7	16	18
65	Nitrate	0	4	16	16
85	Chloride	0	11	20	26
85	Nitrate	0	11	20	24
86	Chloride	0	14	25	28
86	Nitrate	0	16	19	20
183	Chloride	0	21	30	33
183	Nitrate	0	16	23	26

Only Eaton and Sokoloff regarded the reductions as significant; other workers probably have been incorrect in attributing decreases in their own results solely to experimental errors.

At least one of three factors that might lead to incorrect conclusions is involved in much of the previous work; namely, (a) adjudging the contents of the two ions to be insufficient for accurate determination at all dilutions, (b) omission of samples at low moisture contents, where the effect is most pronounced, and (c) experimental and analytical errors involved in the use of inadequate procedures for sample preparation, solution extraction, and analysis. It is concluded both on experimental and theoretical grounds that soluble chloride and nitrate should decrease with increasing moisture content. Eaton and Sokoloff explained the decrease in chloride as a result of "unfree" water in which chloride salts were insoluble or less soluble than in ordinary water, so that the chloride would be-

come more concentrated in the "free" water; with increasing moisture content, the percentage of unfree water of the total moisture would be decreased and accompanied by a decrease in chloride on the oven-dry soil basis. In 1927, Mattson (36) reported that appreciable chloride adsorption by soil colloids occurs at low pH values, but that with increasing pH this becomes a "negative adsorption" due to a Donnan distribution, that is, the chloride concentration is greater in the solution phase than in the diffuse ion swarm layer surrounding the colloidal particle. Toth (56) obtained positive adsorption of chloride by four soil colloids at pH values of 1.6 to 4.0; after removal of iron oxide, the deferrated colloids showed only slight chloride adsorption, and that only in a pH range of 1.6 to 2.0. Davis (13) found NaCl concentration to be greater in the external phase than in the suspension of a bentonite-NaCl system. Walton (58) found that solutions of NaCl, CaCl$_2$, and KCl become more concentrated when added singly to carbonaceous cation-exchange colloids saturated with the respective cations. Bouyoucos (3) on adding KCl solution to quartz flour obtained an increased freezing-point lowering, which he considered evidence that the solution surrounding the particles was more dilute than the bulk of the solution. Mattson and Wiklander (38) postulated that "negative adsorption" may be due to either the existence of unfree water which does not act as a solvent, or to a Donnan distribution of anions between the ion swarm layer of a colloid particle and its external phase. The experimental results on chloride and nitrate presented here confirm the existence of anion gradients within the soil colloidal uspension, but a distinction between the two postulated mechanisms and other possible explanations requires additional evidence from other techniques.

Phosphate. The content of phosphate, the lowest of all ions determined, increases from twofold to 17-fold on dilution from saturation percentage to 500 per cent. These results agree with previous phosphate studies. The increases can be attributed to solution of "insoluble" phosphates by additional water, dilution of soluble calcium and magnesium salts, and anion replacement by hydroxyl ions.

Total salts. For this discussion, "total salts" refers to the higher value between total dissolved cations and anions. The total salts of soils 56, 85, and 86 increased to twofold, ninefold, and fourfold, respectively, on dilution, primarily from solution of gypsum. Those of soils 58 and 183 were doubled, because of the presence of solid-phase carbonates. The total salts of soil 65 appeared virtually constant throughout the moisture range studied. The decrease between 18.4 and 200 per cent moisture amounted to 4.7 per cent. A sample of CaCl$_2$-treated Ritzville loam, not discussed in detail here, contained the following total salts at 38.5, 200, and 500 per cent moisture: 9.77, 9.41, and 9.87 e.p.m. This represents a decrease of 3.7 per cent between 38.5 per cent and 200 per cent moisture. This general agreement on these two naturally leached soils suggests that decreases in total salts can occur on dilution, and understandably so on the basis of principles discussed in this paper.

Exchangeable bases

The exchangeable-base values calculated as explained in the section on methods are shown in figure 7. The base-exchange capacities are 25.9, 8.1, 21.4, 15.3,

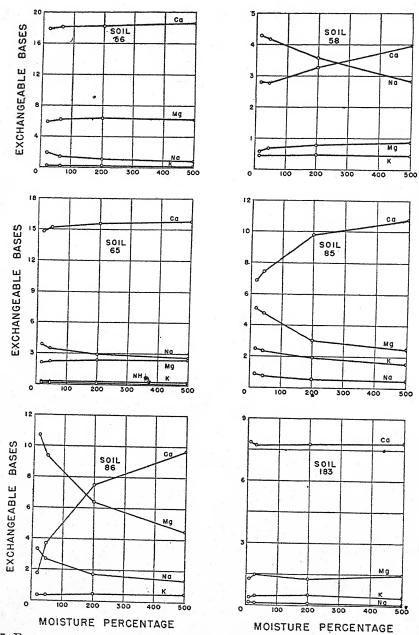Fig. 7. Effect of Moisture Content on Exchangeable Base Status of Six Soils

16.1, and 9.6 m.e. per 100 gm. for soils 56, 58, 65, 85, 86, and 183, respectively. Exchangeable hydrogen has not been included, because in five soils the sum of extracted bases (corrected for soluble ions) exceeded the capacity and in Palouse loam the sum was only 0.1 to 0.2 m.e. below the capacity.   Calcium remained

constant or increased in all soils. In soils 85 and 86, exchangeable Mg was decreased by 51 and 58 per cent (based on the field moisture values) on dilution. Potassium decreased by 37 per cent in soil 85 and increased by 49 per cent in soil 86.

Exchangeable sodium decreased in all soils on dilution by the following percentages: 55, 34, 32, 48, 58, and 50. In similar studies on nine soils, Eaton and Sokoloff (16) found the exchangeable sodium to be reduced by 20 to 94 per cent on substitution of the soluble sodium in 1:5 extracts for that in displaced soil solutions. Many of these reductions occur in ranges of sodium values that are regarded as critical with respect to the physical and nutritional aspects of alkali soils. On further dilution or on leaching, even more sodium is displaced from the soil colloids. Many low or virtually negligible exchangeable sodium values reported in the literature result from such dilution or from prior leaching designed to eliminate the interference of soluble salts. The decrease in sodium and ammonium of soil 65 is attributed to the cation dilution effect wherein soluble calcium and magnesium replace exchangeable sodium and ammonium from the colloids. This mechanism must also operate in the other soils, but the effect is masked by the occurrence of sources of calcium and magnesium other than soluble and exchangeable.

DISCUSSION

The results presented here and those of previous workers illustrate many of the chemical processes which occur on successive additions of water to soil. Some reactions are characteristic of both humid and arid soils, whereas others are more prominent in the latter group because of the greater abundance of soluble materials. That appreciable contents of soluble neutral salts, gypsum, alkaline earth carbonates, and incompletely weathered silicates and other minerals will affect the relationships of dissolved and exchangeable ions is readily predictable. The magnitude of these effects varies with soil characteristics and relative abundance of the various compounds. It is concluded that in arid soils dissolved ions should be determined at or near the moisture content at which the results are to be applied. In a soil the soluble salts of which vary considerably on dilution, the exchangeable-base status also changes on dilution and is correctly estimated only at the moisture content at which the soluble cations are determined.

In addition to the processes which result from the solution of additional materials on dilution, other interesting phenomena which affect the cations and anions of both arid and humid soils exist. The publication by Eaton and Sokoloff (16) of results indicating that on dilution of a soil suspension soluble calcium replaced exchangeable sodium from the base-exchange complex was actually antedated by Gapon (17, 18), who expressed the effect in this manner: In base exchange involving two cations of equal valence, the equilibrium is not affected by addition of water, but if the cations are of different valence, the cation of lower valence is displaced from the adsorbent to an extent that increases with dilution. Further evidence of the cation dilution effect has been presented by Ivanov and Gapon (23), Kurchatov and Kozlikhin (30), and Magistad, Fireman, and Mabry (32).

The soluble and exchangeable base studies on noncalcareous Na-treated Palouse loam demonstrate the dilution effect between the divalent ions calcium and magnesium, on the one hand, and the monovalent ions sodium, potassium, and ammonium, on the other. Mattson and Wiklander (38) discussed the "square-root dilution law" involved in exchange between monovalent and divalent cations on the basis of a Donnan distribution of cations.

The sharp distinction usually made between "soluble" and "exchangeable" cations is somewhat artificial. It has been known that cations vary with respect to the degree of their dissociation from the surface of an electro-negative colloidal particle (24). Marshall (34) obtained measurements on mixed Ca-K-clay systems which indicated that at a pH value of 5.7 the ionic atmosphere contained six times as many potassium ions as calcium ions, and at a pH of 9, about twice as many. In other words, not all the exchangeable cations are held equally tightly, nor are they equally "exchangeable."

From the results of his experiments, Mattson (37) established an anion series based on relative replacing ability, similar to series established for cation exchange, as follows: $OH^- > PO_4^{---} > SiO_3^{--} > SO_4^{--} > Cl^-$. At low pH values at which all these anions are positively adsorbed by soil colloids, a valence dilution effect exists for anions similar to that for cations at higher pH values (39).

Results of Bouyoucos (3), Davis (13), and Walton (58), discussed in the section on chloride and nitrate results, demonstrated the existence of lower anion concentrations in the water immediately surrounding a colloidal particle than in that at a greater distance from it. The quantitative agreement of decreases in soluble chloride and nitrate on dilution in all six soils in the present study suggests that this phenomenon of "negative anion adsorption" may be universal in neutral and alkaline soils. It is not known why Eaton and Sokoloff found a decrease in chloride in only three out of nine soils. The origin of this negative adsorption of anions may lie in "bound water" (7) [which would include salt-free water and water of hydration (13)] or in a diffuse anion swarm the distribution of which depends on a Donnan or other equilibrium mechanism (13, 39). The two concepts probably are not irreconcilable but supplementary, and perhaps are fundamentally identical in some respects. Although Davis (13) has criticized certain ill-founded applications of the Donnan distribution principle, he recognizes the existence of forces in soil colloid systems which cause cation and anion concentration gradients.

As part of a previous study, the soil solution was extracted from a sample of Hesperia sandy loam at the liquid limit (upper plastic limit) by the pressure-membrane method. The solution was analyzed in six fractions, which contained the following total salt concentrations, arranged in the order of extraction: 14.9, 15.8, 15.9, 15.6, 12.3, and 9.5 e.p.m. The corresponding conductivities ($\kappa \times 10^5$ at 25° C.) were 134, 138, 139, 135, 116, and 94. The decrease occurring in the latter part of this extraction is further evidence that the "outer" soil solution is more concentrated than that nearer the soil particles.

These considerations suggest that, provided solubility and other extraneous effects are absent, total dissolved salts should decrease on dilution. In natural

soils, this reduction is masked to varying degrees by the solution of additional solid material by increased quantities of water. In leached soils, the soluble salt concentration is so low, and difficult to analyze accurately, that the solution of soil minerals on dilution results in an apparently constant or an increased dissolved salt content. In naturally saline soils which contain sufficient salts for accurate analysis, the solution of silicate minerals, carbonates, and gypsum, and ionic exchange reactions combine to produce increased dissolved salts on dilution. The artificially salinized sample of Palouse loam showed no increase, and possibly a decrease over part of the moisture range, as did a sample of Ritzville loam treated with $CaCl_2$. It is believed that dilution of a slightly saline neutral soil, virtually free of slightly soluble compounds, adsorbed anions as sulfate, phosphate, and bicarbonate, fixed K, and similar components, and containing only one neutral salt, such as $CaCl_2$, would involve a decrease in that salt similar in magnitude to that obtained for decreases in chloride and nitrate in this investigation.

SUMMARY

Dissolved ions of six soils were determined at four moisture contents, field moisture, saturation percentage, 200 per cent, and 500 per cent. The three dilute suspensions were prepared from the field moisture sample by addition of calculated increments of water. The ions included Ca, Mg, Na, K, NH_4, CO_3-HCO_3, SO_4, Cl, NO_3, and PO_4. The soils contained varying quantities of soluble salts, alkaline earth carbonates, and gypsum. The exchangeable base status at each moisture content was determined by ammonium acetate extraction and calculations based on information on cation-exchange equilibriums.

With the exception of sulfate in one soil, the soluble contents of all ions in all soils changed to some degree on dilution. Sodium, K, NH_4, CO_3-HCO_3, PO_4, and SO_4 (with the exception mentioned) increased in all soils with increasing moisture content. Calcium and magnesium increased in four soils, passed through maxima in one soil, and decreased continuously in one. The increases in these eight ions are explained by ion exchanges and solution of solid compounds by additional amounts of water. The decreases in Ca and Mg result from a cation valence dilution effect whereby, on dilution, soluble Ca and Mg replace exchangeable Na, K, and NH_4 from the soil colloids. Chloride and nitrate decreased continuously in all soils; the average reduction in the two ions was 28 and 23 per cent, respectively. These anion decreases may possibly result from the existence of unfree water, negative adsorption of monovalent anions in neutral and alkaline soils, or a combination of the two mechanisms.

Exchangeable sodium decreased continuously on dilution, by percentages ranging from 32 to 58. The ratio of exchangeable calcium to magnesium in the two gypsiferous soils increased tremendously on dilution. It is recommended that the soluble salts of arid soils be determined at a moisture content near that at which the results are to be interpreted. In soils having appreciable contents of mixed soluble salts, the determined exchangeable-base status applies only to the moisture content at which the soluble salts are determined. The theoretical and experimental aspects of the various cation and anion phenomena lead to the

conclusion that the soil solution cannot be homogeneous throughout its entire mass and generally is less concentrated near the soil colloidal particles.

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CHANGES IN CONSTRUCTION OF SOIL MOISTURE TENSIOMETERS FOR FIELD USE

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Richards[2] has described the construction of soil moisture tensiometers. He recommended the use of mercury manometers or vacuum gauges for indicating the soil moisture tension. During the last 2 years the authors have made extensive use of tensiometers in field experiments. For our purposes the vacuum-gauge type was found to be unsatisfactory because of the sluggishness of response and the difficulties in maintenance. Tensiometers of the mercury-manometer type have proved very useful for following soil moisture changes over the range of tension in which they function. There is one practical difficulty, however, in the use of tensiometers of this type in field experiments with row crops requiring cultivation. Such tensiometers are 3 to 4 feet tall, and cultivating implements cannot pass freely over them. Since in any experiment it is desirable to hold constant all factors except those varied intentionally, the area immediately about the tensiometer installation should be cultivated in the same manner as other areas. This is particularly true in irrigated regions, where cultivation often markedly affects water penetration. It is not practical to remove and reinstall the tensiometers at each cultivation, for these operations are troublesome and time-consuming; in addition, their effects upon the roots in proximity to the tensiometer cup and upon equilibrium conditions are not known. It is the purpose of this paper to describe changes in mercury manometer tensiometer construction which facilitate cultivating operations with the tensiometer in place.

Figure 1 shows the details of the changes in construction of the tensiometer, which permit laying the top portion over to the ground, thus enabling cultivating implements to pass over it. The channel iron supporting the capillary tube and graduated metal scale is hinged just above the mercury pot. Opposite the hinged joint an 8-inch length of flexible tubing is inserted in the copper capillary tube. For this purpose a $\frac{1}{8}$-inch I.D. flexible metal tube (RW-91 Rex-Weld braided bronze hose with helical corrugations, manufactured by Chicago Metal Hose Corp., Maywood, Illinois) is recommended, but Koroseal tubing of similar inside diameter can be used. A steel bar $4\frac{1}{2}$ by $\frac{1}{2}$ by $\frac{1}{8}$ inches is attached by screws to the upper part of the channel iron support; when secured by the cotter key as shown in figure 1A this bar locks the tensiometer in the vertical position. As shown in figure 1B, one coil is made in the copper capillary tube at the top

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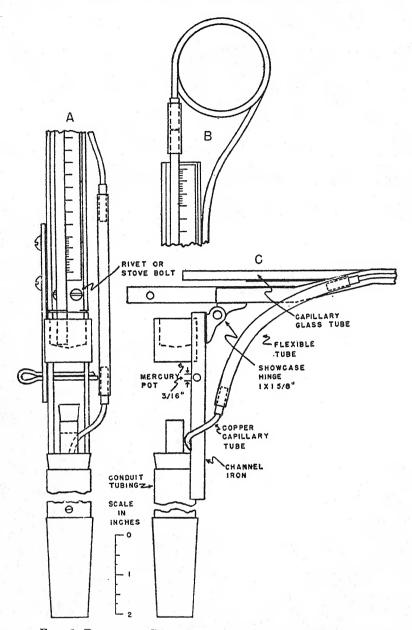
FIG. 1. DETAILS OF CHANGES IN TENSIOMETER CONSTRUCTION

A, front view; B, coil in copper capillary tube at top of tensiometer; C, side view, with tensiometer top lowered to permit passage of tillage implements.

of the tensiometer. This provides sufficient displacement for the raising of the ends of the capillary glass tubing above the mercury pot. A displacement of about an inch is essential when it is necessary to bend the top of the tensiometer

to the ground. Since the glass tubing is held loosely in the channel iron support by means of wire clips, it is relatively easy to displace it up and down. Before bending the top of the tensiometer, as shown in figure 1C, it is necessary to remove the rubber stopper from the air trap in order that the mercury may run back into the mercury pot from the capillary glass tube. After this is done and the cotter key is removed, the top of the tensiometer can be laid to the ground and the cultivating implement can then pass over it freely. After the cultivation is completed, the top of the tensiometer is returned to the vertical position, the cotter key is inserted, and the tensiometer is reset. After 12 to 24 hours, accurate readings can again be taken.

Richards recommended the use of copper capillary tubing of 0.04 inch I. D. He has mentioned the "thermometer effect" of the water column in the capillary tubes. Assuming that neither the copper nor the glass capillary tubes expand with temperature change, it can be shown by calculation that, in going from a temperature of 68° F. to 95° F. the expansion of water in 8 inches of $\frac{1}{8}$-inch I. D. flexible tubing would depress the mercury column in a 1.5-mm. glass tube by 0.34 cm. more than the expansion in a similar length of 0.04-inch I. D. tube. This depression would be equivalent on the graduated scale to 4.3 cm. of water, an amount of no consequence in field work.

STRAW MULCH FOR SOIL IMPROVEMENT

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The use of straw as mulching material has been under investigation at the Oregon Agricultural Experiment Station for the last 5 years and has shown marked improvement in the granulation of the soil (4). The present paper reports the results of further investigation of the effects of straw mulch on the productive capacity of the soil and its response to fertilizer treatments.

METHODS

The plan of the treatments of the plots from which soil was used for this study was presented in a previous paper (4). On the straw-mulched plot, the wheat straw was maintained at a depth of 6 inches throughout the 5 years. The sod was the volunteer growth of weeds and grass. From the scraped plot, all surface growth was removed in April, and scraping with a hoe was repeated as often as necessary to prevent growth.

In March 1944, just previous to abandonment of the plots, soil samples were taken as follows: at the 0–1-inch depth, under sod and from the scraped and the straw-mulched plots; at the 1–2-inch depth, from the scraped and the straw-mulched plots. The sod plot was destroyed before the sample of the 1–2 inch depth could be taken.

Mammoth Russian sunflowers, as an indicator plant, were grown on these soils in the greenhouse to determine the fertility level of the soil in the different plots and to measure the response to fertilizer treatment.

Samples of soil, each weighing 500 gm., were weighed into No. 2 charcoal-plate fruit cans, lacquered inside. Trials were in quadruplicate, five plants per can, making 20 plants receiving each treatment. The fertilizer treatments, indicated in table 1, were mixed with half the soil, and the mixture was placed in the bottom of the can. The unfertilized soil occupied the upper half of the can. Several sunflower seeds were planted April 27 in the upper soil, and measured quantities of water were applied daily or as often as needed to maintain growing conditions. The sunflowers were thinned to five plants of uniform size per can when they had two fully developed leaves. They were grown to near the blossoming stage, then harvested, dried, and weighed. The growth period was 7 weeks.

The chemical studies were made on the soil after the crop was grown and harvested. The entire amount of soil in the can was mixed before sampling for analysis. Soluble potassium was removed from the soil by treating 10 gm. with 150 ml. of 0.05 N HCl, warmed to about 60° C., for 15 or 20 minutes. The extract was filtered by suction on a Gooch crucible. An additional 350 ml. of cold acid, in small portions, was leached through the soil, each portion being

TABLE 1

Dry weight of 20 sunflower plants (5 in each of 4 cans) grown in soils fertilized with a 13-16-12 fertilizer at rates of 1,000 to 4,000 pounds per 2,000,000 pounds of soil

DEPTH OF SOIL LAYER	PLOT TREATMENT	TOTAL DRY WEIGHT OF 20 SUNFLOWER PLANTS FERTILIZED AT DIFFERENT RATES						RELATIVE AVE. YIELDS
		Check— no fertilizer	1,000 lbs. fertilizer	2,000 lbs. fertilizer	3,000 lbs. fertilizer	4,000 lbs. fertilizer	Average	
inches		*gm.*	*gm.*	*gm.*	*gm.*	*gm.*	*gm.*	*per cent*
0–1	Sod	12.5	20.9	22.8	20.4	25.5	20.4	130
	Scraped	8.5	16.2	18.8	17.3	17.5	15.7	100
	Straw mulch	23.2	29.7	32.1	32.8	33.3	30.2	192
1–2	Scraped	10.1	16.5	19.2	16.1	16.5	15.7	100
	Straw mulch	18.3	24.4	28.5	27.5	31.5	26.0	166
Average..................		14.5	21.5	24.3	22.8	24.9		

TABLE 2

Increase in dry weight of 20 sunflower plants fertilized at different rates, over unfertilized plants in same soils

DEPTH OF SOIL LAYER	PLOT TREATMENT	INCREASE IN WEIGHT OF 20 SUNFLOWER PLANTS FERTILIZED AT DIFFERENT RATES					RELATIVE YIELDS UN- FERTILIZED
		1,000 lbs. fertilizer	2,000 lbs. fertilizer	3,000 lbs. fertilizer	4,000 lbs. fertilizer	Average	
inches		*gm.*	*gm.*	*gm.*	*gm.*	*gm*	*per cent*
0–1	Sod	8.4	10.3	7.9	13.0	9.9	147
	Scraped	7.7	10.3	8.8	9.0	9.0	100
	Straw mulch	5.5	8.9	9.6	10.1	8.5	273
1–2	Scraped	6.4	9.1	6.0	6.4	7.0	119
	Straw mulch	6.1	10.2	9.2	13.2	9.7	215
Average..................		6.8	9.8	8.3	10.3		

allowed to drain thoroughly before the next portion was added. The potassium in the leachate was determined as the cobaltinitrite by the method of Hibbard (3), asbestos oxidized with permanganate being used for filtering to separate the precipitate from the leachate. Soluble phosphorus was determined by the method of Truog (5). Nitrates were determined with phenoldisulfonic acid, organic matter by the method of Walkley and Black (6), and aggregates larger than 1.0 mm. diameter by the wet-sieve method as reported by the authors (4).

RESULTS

The growth of sunflowers in the soil from the first inch of the plot that had received a straw mulch was superior to that obtained in the other soils. The seed germinated more quickly and the plants were more vigorous from the start. Dry weights of these plants (table 1) averaged 50 per cent more than those of plants grown in soil from the sod plot and were nearly twice those obtained in

TABLE 3

Soluble phosphorus content of soil under various treatments

Determined after crop was grown

DEPTH OF SOIL LAYER	PLOT TREATMENT	SOLUBLE PHOSPHORUS IN SOIL FERTILIZED AT DIFFERENT RATES					
		Check—no fertilizer	1,000 lbs. fertilizer	2,000 lbs. fertilizer	3,000 lbs. fertilizer	4,000 lbs. fertilizer	Average
inches		*p.p.m.*	*p.p.m.*	*p.p.m.*	*p.p.m.*	*p.p.m.*	*p.p.m.*
0–1	Sod	163	167	206	206	206	190
	Scraped	191	206	215	229	215	211
	Straw mulch	166	191	212	228	217	203
1–2	Scraped	169	179	206	200	218	194
	Straw mulch	141	176	253	226	308	221
Average....................		166	184	218	218	233	

TABLE 4

Soluble potassium content of soil under various treatments

Determined after removal of crop

DEPTH OF SOIL LAYER	PLOT TREATMENT	POTASSIUM REMOVED, BY LEACHING WITH 0.05 N HCl. FROM SOIL FERTILIZED AT DIFFERENT RATES					
		Check—no fertilizer	1,000 lbs. fertilizer	2,000 lbs. fertilizer	3,000 lbs. fertilizer	4,000 lbs. fertilizer	Average
inches		*p.p.m.*	*p.p.m.*	*p.p.m.*	*p.p.m.*	*p.p.m.*	*p.p.m.*
0–1	Sod	174	186	149	286	274	214
	Scraped	273	224	283	207	293	256
	Straw mulch	448	423	448	398	485	440
1–2	Scraped	224	199	211	174	199	201
	Straw mulch	448	423	398	323	398	398
Average....................		313	291	298	278	330	

soil from the scraped plot. The dry weights of plants grown in the soil from the second inch of the mulched plot were not so great as were those of plants grown in soil from the first inch. The yields in soil from the first and the second inch of the scraped plot were about the same. The approximate maximum yield was produced in most cases from the 2,000-pound rate of fertilization using a 13–16–12 mixture made up from ammophos 16–20 and muriate of potash. The yield increases caused by the fertilizer treatment were rather uniform (table 2). The

scraped plot was much the lowest in yield without fertilizer and maintained the same relative position when fertilized. The straw-mulched soil was much the heaviest yielder without added fertilizer, but showed no greater increase from the use of fertilizer than did the other plots.

Analysis of the soil indicated that the addition of the fertilizer increased the soluble phosphorus (table 3).

TABLE 5

Organic matter content of soil from sod, mulched, and scraped plots
Determined after cropping in the greenhouse

DEPTH OF SOIL LAYER	ORGANIC MATTER CONTENT OF SOIL		
	Sod plot	Scraped plot	Straw-mulched plot
inches	*per cent*	*per cent*	*per cent*
0–1	4.53	4.01	7.78
1–2	3.40	3.26	5.52

TABLE 6

Effect of straw mulch on production of aggregates larger than 1 mm. in diameter

DEPTH OF SOIL LAYER	PLOT TREATMENT	AGGREGATES LARGER THAN 1 MM. IN WHOLE SOIL FERTILIZED AT DIFFERENT RATES						RELATIVE AVERAGE AGGREGATION
		Check— no fertilizer	1,000 lbs. fertilizer	2,000 lbs. fertilizer	3,000 lbs. fertilizer	4,000 lbs. fertilizer	Average	
inches		*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
0–1	Sod	14.3	17.2	17.8	20.2	16.3	17.2	50.6
	Scraped	3.8	2.9	2.2	4.0	2.5	3.1	9.1
	Straw mulch	27.9	31.8	38.2	36.1	35.8	34.0	100.0
1–2	Scraped	1.3	2.0	1.4	1.7	2.2	1.7	5.0
	Straw mulch	15.1	18.3	18.9	16.0	15.4	16.7	49.1
Average...............		12.5	14.4	15.7	15.6	14.4		

Soluble potassium (table 4) was considerably the highest from the straw-mulched soil. Feztilizer, however, had little effect on the soluble potassium in any of the plots.

Since no more than 1 or 2 p.p.m. of nitrates were found in any of the soils, the results are not reported. The humus content of the soil from the straw-mulched plot was definitely the highest (table 5). An outstanding difference was also found in the proportion of soil in aggregates larger than 1.0 mm. diameter (table 6).

DISCUSSION

Application of a deep straw mulch imparted to the soil in 5 years' time far greater productive capacity than could be explained entirely by the nutrients

contributed to the soil. Part of the good effect of the straw was undoubtedly physical, since soil granulation was greatly improved.

The relatively large amounts of soluble phosphorus found would indicate that there was probably no lack of this element, even in the unfertilized soil, and that the soil from the mulched plot probably did not supply any more soluble phosphorus to the plants than did the other plots. Likewise, the rather liberal amounts of soluble potassium found indicate that this element probably was not controlling production.

Since the previous study (4) indicated that the straw-mulched soil during the third year of the 3-year period was producing a considerable amount of nitrate (4 to 29 p.p.m. in the soil), it is probable that better nitrogen nutrition was partly responsible for the good growth on the straw-mulched plot. The high humus level of this plot would appear to be a favorable factor. The straw had apparently been on the plot long enough for the first depressing effect of a high-carbon material to disappear. Since the plants were destroyed before an analysis of the material was considered, it was impossible to determine how much nitrogen was taken up by the plants.

Physical soil changes caused by the straw were undoubtedly favorable for plant growth. While the plants were being grown, the soil granules became progressively more dispersed in the soil from the scraped plot, until watering caused the surface of the soil to become soupy in consistency. Water would penetrate only about 2 inches in 4 hours, unless a hole was made with a stick to let the water down. The straw-mulched soil, on the other hand, remained granular and porous, and water penetrated the entire depth almost at once. The sod soil was about midway between the other two in aggregate analysis, general appearance, and yield of plant growth. This difference in the physical behavior of the soils, since it must have influenced the nutrition of the plants through the effects on soil aeration, is the most apparent partial explanation for the outstanding yield differences on the soils with the different treatments. Other factors, such as nutrient delivery by the soil to the plant, doubtless also affected the nutrition of the plants. The effects of physical and of chemical changes in the soils brought about by mulching with straw cannot be evaluated separately but are very pronounced as indicated by plant yields.

Gourley (1) has discussed the improvement of orchard soils under a mulch system from the standpoint of nutrient supply. He pointed out that there may be abundance of both minerals and nitrates under a mulch after a period of time and that growth of trees is excellent. He reported more nitrates under legume mulch than under straw mulch, and suggested that a legume mulch may have to be avoided because of too much nitrate. Havis (2) found that a straw mulch was effective in producing aggregates of the larger sizes. Evidence therefore indicates that soils are improved for plant growth under deep straw mulch as a result of favorable changes in the soil that are both chemical and physical.

CONCLUSIONS

Growth of sunflower as an indicator plant in soil taken from the top 2 inches under a straw mulch was appreciably greater than in soil taken from sod or a scraped plot.

The straw-mulched soil maintained its lead in promoting plant growth after liberal fertilization of all the soils to correct nutrient deficiencies.

The straw-mulched soil contained the most acid-soluble potassium, was richest in humus, and had much the highest proportion of aggregates larger than 1.0 mm. diameter.

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THE INTEGRATED SOIL MOISTURE STRESS UPON A ROOT SYSTEM IN A LARGE CONTAINER OF SALINE SOIL

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Several factors are operative in the study of plants grown in cultures of saline soil which limit the interpretation of the observed results. These include variability of salt distribution in the soil, variation in moisture distribution at a given time as a result of variability in rate of water removal by various parts of the root system, and variability in the total moisture content of the soil with time. It is preferable to consider plant response to soil moisture conditions in terms of a concept of free energy. Hence, there arose a need for a method which would permit the above variables to be taken into account in evaluating plant response in terms of the energy content of the water being absorbed. This paper presents a mathematical approach to such a method.

It is known that soil moisture percentage cannot be maintained at a constant value when the percentage is below field capacity (8), even though numerous experiments in which this feature was postulated have been conducted. The soil moisture regime in large containers of soil is preferably maintained by adding sufficient water at an irrigation to wet the whole soil mass to field capacity and then by permitting the plant to remove a specified proportion of the available water (that in excess of the permanent wilting percentage). The tension on the soil moisture at field capacity lies within the range of 0.1–0.4 atmosphere (14). Values for the soil moisture tension over the wilting range may vary widely, but the 15-atmosphere-percentage almost invariably falls within this range (14). Even though this wide diversity in tension is found over the range of available moisture, it is frequently considered to be equally available throughout this range. The tenability of this postulate rests with the hyperbolic nature of the relationship between soil moisture percentage and tension (16, 17). In other words, the soil moisture tension in most soils does not exceed 1 atmosphere until most of the available water is removed, but a tremendous increase in tension takes place with removal of the last portion of the available water.

It is known that there are two groups of forces contributing to the decrease in the free energy of soil moisture: (a) the forces (hydrostatic, gravitational, adsorptive) which induce a tension upon the soil water; and (b) the osmotic forces due to dissolved solids in the soil solution (2, 4, 14). As Richards and Weaver (14) have pointed out, most discussions of the free energy of soil moisture have given inadequate treatment of the osmotic effects. They reported that soil moisture retention data derived from tensiometers or from pressure-plate

(13) or pressure-membrane (12) apparatus should be supplemented by a determination of the osmotic pressure of the soil solution in order to arrive at an evaluation of the energy relations of the soil moisture. Their studies indicated that the summation of the osmotic pressure of the soil solution plus the moisture tension at the permanent wilting percentage for many different soils covered a narrower range than did the corresponding values for moisture tension alone. Wadleigh and Ayers (17) related this summation of the two groups of forces to the growth of beans in saline soil. For convenience they designated the aforementioned summation as the "total soil moisture stress."

Thus, letting S designate the total stress in atmospheres,

$$S = T + \pi \qquad (1)$$

where T designates the soil moisture tension in atmospheres, and π the osmotic pressure of the soil solution in atmospheres.

Obviously,

$$T = f(P_w) \qquad (2)$$

and

$$\pi = f(P_w) \qquad (3)$$

where P_w is the soil moisture percentage. It is evident, therefore, that as a plant removes water from a soil, the water stress upon the root system is continually increasing. Since this stress cannot be maintained constant, the rate of change of stress with time should be ascertained.

The situation is further complicated in a saline soil by the fact that it is not possible for liquid water to move into and through a soil without carrying soluble salts with it. Consequently, if the container of soil is surface-irrigated, as is usually the case, solutes will tend to accumulate in the lower strata of soil. This means that at constant soil moisture percentage throughout the soil mass there would be an increase in the osmotic pressure of the soil solution from the surface downward (1). Under such a condition, even though the roots thoroughly permeate the soil mass there will be an unequal removal of soil moisture from different strata, the rate of removal being lowered as osmotic pressure of the soil solution increases. This is in accordance with observations from controlled experiments showing that rate of water absorption by plant roots is inversely related to the osmotic pressure of the substrate (5, 6, 7, 9). Such data enhance the validity of the main assumption made in the following presentation. That is, it is assumed that as water is removed from the soil mass, the total stress on the water being absorbed at a given time tends to approach uniformity in all the various strata of soil, even though the components of the total stress—osmotic pressure and tension—vary considerably among these strata.

In studies of plant response to soil salinity at this laboratory, the plants are usually grown in steel drums holding approximately 100 pounds of dry soil. The depth of the soil in the containers averages about 15 inches. These containers are weighed daily so that information is available on the rate of water loss from the soil by evaporation and transpiration. When the weight of the drum of soil indicates the need of water, enough water is added to bring the whole soil mass to approximately the field capacity.

In order to evaluate the interrelationship of salt concentration and soil moisture tension upon plant response, it would be helpful to know the moisture stress upon the plant between irrigations for a given experimental treatment. In addition to knowledge of the average stress upon the plant during the irrigation interval, information should be available as to the magnitude of the total stress at various times during this period.

Let t designate the time in days of the irrigation interval, and A the integrated atmosphere-days, then,

$$A = \int_{t_o}^{t_x} S \, dt \tag{4}$$

The average soil moisture stress during the irrigation interval is then equal to $\frac{A}{t_x}$, where t_x is the number of days in the interval.

To integrate,

$$S = f(t) \tag{5}$$

must be substituted in the above integral. This relationship cannot be directly evaluated and must be derived. The data obtained by daily weighing the soil containers permits a direct formulation of the relationship,

$$W = f(t) \tag{6}$$

where W designates the amount of water present in the soil. The relationship

$$S = f(W) \tag{7}$$

needed in order to convert the relation in equation (6) to that of (5) may be derived from the known physical characteristics of the soil and the distribution of salt in the container. It should be emphasized that water removal from the soil is assumed to be so distributed as to tend to make S uniform throughout the absorbing root zone at any particular time.

The calculations involved are exemplified by data from an actual experiment in which the growth of guayule as affected by varying degrees of salinity of Panoche loam was studied (18). For the soil used, the relation between tension and soil moisture percentage was that shown in figure 1[2]. The hyperbolic relation of equation (2) can be formally expressed by the empirical equation,

$$T = \frac{K}{P_w^n} = \frac{3.35 \times 10^7}{P_w^{6.83}} \tag{8}$$

in which K and n are constants.

Prior to displacing the soil solution from the soil samples taken from different strata in the container, the soil moisture percentage was adjusted to approximately 12. The solution was displaced by means of a pressure-membrane apparatus (10, 12) and the osmotic pressure of the solution was determined cryoscopically.

[2] The author is indebted to Milton Fireman for these data.

The small deviations in actual percentage of moisture from 12 per cent moisture at time of displacement were taken into account by an adjustment of the osmotic pressure values. The relation of equal (3) was then evaluated as

$$\pi = \frac{12Q}{P_w} \qquad (9)$$

where Q is the osmotic pressure of the soil solution when P_w equals 12. Equation (9) does not take into account variations in total amount of dissolved material with variations in P_w. This is not a serious deficiency with the possible exception of gypsiferous soils (11).
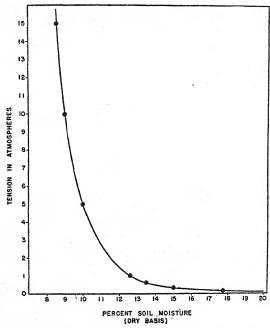
FIG. 1. RELATION BETWEEN MOISTURE TENSION AND MOISTURE PERCENTAGE OF A SAMPLE OF PANOCHE LOAM

Equation (1) may now be expressed as

$$S = \frac{3.35 \times 10^7}{P_w^{6.83}} + \frac{12Q}{P_w} \qquad (10)$$

This relationship is shown in figure 2.

It would be very convenient if equation (10) could be rearranged to express P_w as an explicit function of S and Q. Since the exponent of equation (8) may not be a whole number and may be a high power, this is not always possible. Equation (10) may, however, be rearranged so that Q is expressible as an explicit function of S and P_w thus,

$$Q = \frac{SP_w^{6.83} - (3.35 \times 10^7)}{12P_w^{5.83}} \qquad (11)$$

At constant values of S, values of Q may be calculated for a series of values of P_w. These values of P_w may then be plotted as functions of the derived values of Q as shown in figure 3. The relationships shown in this figure may then be derived empirically in such manner that P_w is expressed as an explicit function of S and Q. This relationship could not be expressed by an equation linear in its constants, or even one which was linear when converted to the logarithmic form. Hence, the method of least squares could not be used. The method
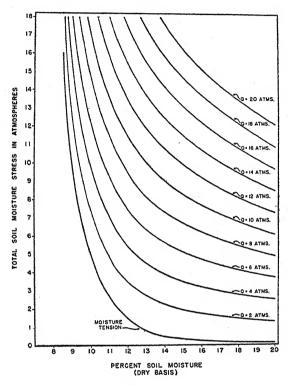
FIG. 2. RELATIONSHIP BETWEEN SOIL MOISTURE STRESS AND MOISTURE PERCENTAGE WITH THE SALT CONTENT AT DIFFERENT Q VALUES IN A SAMPLE OF PANOCHE LOAM

described by Scarborough (15, p. 374) for nonlinear formulas produced an equation for figure 3 which expressed the relationships with a high degree of precision. Thus,

$$P_w = \frac{12.6}{S^{0.145}} + \frac{2Q}{S} + \frac{1.14Q^{2.75}}{S^{2.5}} \qquad (12)$$

In the evaluation of equation (7) between S and W, it is necessary to consider that

$$W = \frac{1}{100} \int_{V_o}^{V_x} P_w \, dV \qquad (13)$$

where V is the mass of soil in pounds.

In the experimental data used, the containers held 100 pounds of dry soil, and the soil mass was 15 inches in depth. Empirically then,

$$V = \frac{100}{15} D = 6.7 D \qquad (14)$$

where D is the depth of the soil in inches.

Substituting equations (12) and (14) into equation (13), the latter becomes

$$W = \frac{6.7}{100} \int_{D_o}^{D_x} \left[\frac{12.6}{S^{0.145}} + \frac{2Q}{S} + \frac{1.14Q^{2.75}}{S^{2.5}} \right] dD \qquad (15)$$
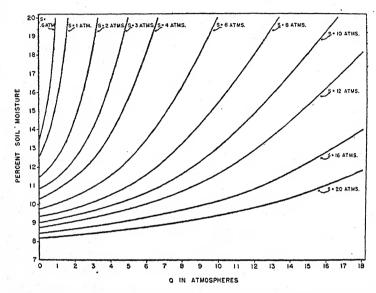
FIG. 3. DATA OF FIGURE 2 REARRANGED SO THAT P_w IS EXPRESSED AS A FUNCTION OF Q AT DIFFERENT VALUES OF S

In this equation, it should be recalled that S is a constant. In order to integrate, the proper functional evaluation of D must be substituted for Q. Figure 4 shows a typical relationship between Q and depth in the container. Since this curve is parabolic, substituting the function of D for Q in equation (15) would lead to mathematical difficulties, that is, it would lead to the expansion of a quadratic equation to a fractional power. However, D may be expressed as an empirical function of Q. For the curve in figure 4, this was found to be,

$$D = -4.32 + 11.6Q - 1.69Q^2 \qquad (16)$$

Hence,

$$dD = (11.6 - 3.38Q) \, dQ \qquad (17)$$

and this may be substituted into equation (15),

$$W = \frac{6.7}{100} \int_{Q_1}^{Q_2} \left(\frac{12.6}{S^{0.145}} + \frac{2Q}{S} + \frac{1.14Q^{2.75}}{S^{2.5}} \right)(11.6 - 3.38Q)\, dQ \qquad (18)$$

The limits of integration, Q_1 and Q_2, in equation (18) may be found as follows:

Q_1 is the value of Q at the surface of the container and is derived from equation (16) by setting D equal to 0 and solving quadratically. In the present example, $Q_1 = 0.4$.

Q IN ATMOSPHERES
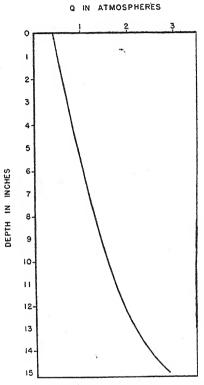
FIG. 4. OBSERVED RELATIONSHIP BETWEEN Q AND DEPTH IN A LARGE CONTAINER OF PANOCHE LOAM

Q_2, similarly, is the value of Q at the base of the container and is derived quadratically from equation (16) by setting D equal to 15, except when S is considered at a sufficiently low value that water is theoretically not removed from the lower strata. In the soil under consideration the field capacity was approximately 20 per cent. At each irrigation, sufficient water was added to bring the entire soil mass to 20 per cent soil moisture. Then, at a given value of S, equation (11) shows that

$$Q_2 = \frac{S \times 20^{6.83} - (3.35 \times 10^7)}{12 \times 20^{5.83}} \qquad (19)$$

If S in the present example is taken as 1, then $Q_2 = 1.6$.

It should be noted further, that the integration of equation (*18*) between the limits of 0.4 and 1.6 does not include soil moisture in the drum below the horizon where Q equals 1.6. Substituting this value in equation (*16*), it is found that D equals 10.1 inches. Thus, when S is taken as 1 atmosphere, there will be, according to equation (*18*), 10.43 pounds of water in the surface 10.1 inches of soil. The lower 4.9 inches of soil must be assumed to contain 20 per cent moisture, since this is the value to which it was adjusted on irrigation and no water was removed from this lower horizon on the development of a water stress of 1 atmosphere. Hence, there will be $20 \times \dfrac{4.9}{15} = 6.53$ pounds of water in the lower 4.9 inches of soil. Total soil moisture present in the drum of soil is 10.43 + 6.53 = 16.96 pounds of water.
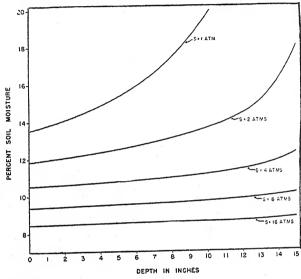
FIG. 5. RELATIONSHIP BETWEEN P_w AND DEPTH IN THE CONTAINER OF SOIL AT VARIOUS VALUES OF S

The relation between percentage of soil moisture and depth in the container is shown in figure 5 for various values of S. These curves were derived by use of figure 3. Thus, for a given value of S, values of P_w may be taken off these curves for selected values of Q as follows:

Values of P_w *at Given Values of* Q

S \ Q	0.4	0.8	1.2	1.6	2.0	2.4	2.8
1	13.6	15.0	16.7	20.0			
2	11.8	12.3	13.0	13.7	14.6	15.8	17.4
4	10.5	10.7	10.9	11.2	11.5	11.8	12.2
8	9.4	9.5	9.6	9.7	9.8	10.0	10.1

From figure 4, the values of D for corresponding values of Q may be derived. For the above selected values of Q, D would be as follows:

Q	0.4	0.8	1.2	1.6	2.0	2.4	2.8
D	0	3.8	7.3	10.3	12.4	13.8	14.8

By substituting these values of D for corresponding values of Q in the previous tabulation, the relationships shown in figure 5 are obtained. It is evident that
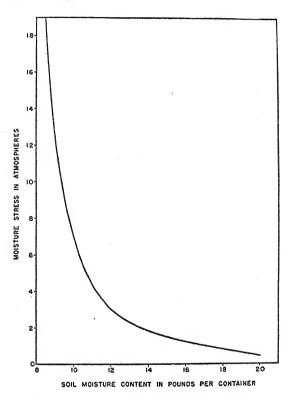
FIG. 6. DERIVED RELATIONSHIP BETWEEN SOIL MOISTURE STRESS AND SOIL MOISTURE CONTENT FOR THE SPECIFIED OBSERVATIONS ON SALT DISTRIBUTION FOR A CONTAINER OF PANOCHE LOAM

the area under a given S curve may be integrated by Simpsom's rule, permitting the derivation of the average percentage of water present in the soil. Since there is 100 pounds of soil in the container, values for average percentage of soil moisture are numerically equal to pounds of water present in the soil. In other words, values of W for given values of S may be derived graphically in addition to the more involved, yet more precise, integration.

The relation between W and S found by substituting various values for S in equation (18) is a generalized form for a given soil, but the relation in figure 6 is virtually specific for a given container of soil because of specificity in salt

distribution. The labor involved in deriving the constants for the equation of such a relationship is not warranted.

The relation of equation (6), $W = f(t)$, is shown in figure 7. As mentioned previously, these data were obtained by weighing daily the containers of soil. The relationship in figure 6, where $S = f(W)$, may be transformed by way of that in figure 7, to develop the relation in figure 8, wherein $S = f(t)$, equation (5). This exponential curve would have to be formally expressed in order to integrate by means of equation (4). However, integration of the area between t_o
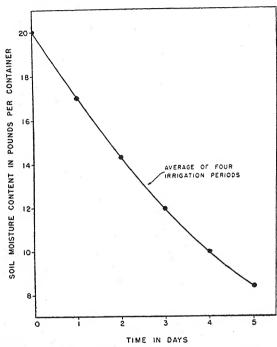
FIG. 7 OBSERVED RATE OF CHANGE IN MOISTURE CONTENT OF THE SOIL IN THE CONTAINER DURING AN IRRIGATION INTERVAL

and t_5 in figure 8 may be performed quite adequately by Simpsom's rule (19). Thus, equation (4) becomes

$$A = \int_{t_o}^{t_x} S \, dt = \frac{\Delta t}{3} \left[(S_o + S_n) + 4(S_1 + S_3 + S_5 -) + 2(S_2 + S_4 + S_6 -) \right] \quad (20)$$

wherein $\dfrac{t_x - t_o}{\Delta t}$ equals an even number.

In the present example, Δt is taken as 0.5. From the data of figure 8 in which t_x equals 5,

$$n = \frac{5 - 0}{0.5} = 10$$
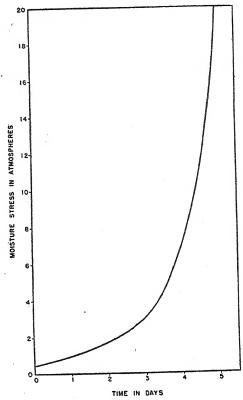
FIG. 8. DERIVED RATE OF CHANGE IN MOISTURE STRESS UPON THE ABSORBING ROOTS OF PLANTS REMOVING WATER FROM SOIL AT THE RATE SHOWN IN FIGURE 7

Thus the following paired values were observed in figure 8:

	S_0	S_1	S_2	S_3	S_4	S_5	S_6	S_7	S_8	S_9	S_{10}
t..	0	0.5	1	1.5	2	2.5	3	3.5	4	4.5	5.0
S.	0.4	0.65	1.0	1.3	1.7	2.2	3.0	4.5	6.9	10.6	20

By substituting the above data in equation (20), it is found that

$$A = 20.4 \text{ atmosphere-days}$$

The average stress per day will then be equal to A/t_x.

$$\frac{A}{t_x} = \frac{20.4}{5} = 4.08 \text{ atmospheres.}$$

SOURCES OF ERROR

The foregoing discussion would not be complete without a consideration of the sources of error. These errors may be considered in four groups:

1. Constancy of the moisture-retention curve.
2. Change in absolute amount of solute with change in soil moisture percentage.
3. Variability in salt distribution within the soil.
4. Certain imponderables with respect to the behavior of the root system.

With respect to the first group, it is known that the locus of the moisture retention curve may be shifted in accordance with the previous treatment of the soil (13). This is especially the case in the lower range of tensions, which reflect the status of the larger pore spaces in the soil. In other words, the structure of the soil is a major factor in determining the locus of this curve at the lower values of tension. Differential treatment of a soil may readily induce changes in structure. Fortunately, however, this source of error is of minor importance with respect to the present thesis, since the variation occurs mainly at the low tension values.

Regarding the second source of error, it must be admitted that $d\pi/dP_w$ may not follow simple dilution or concentration. Thus, in a gypsiferous soil, the soil solution will be saturated or nearly saturated with $CaSO_4$ regardless of P_w. This may bring about appreciable variation in the absolute amount of solute in the soil solution of a given mass of soil at different moisture percentages. Reitemeier (11) has studied this effect in detail. He found that concentration of the various ions in the soil solution is virtually never exactly the inverse of the soil moisture content. If NaCl is the major solute present in the soil solution, however, as is frequently the case in saline soils, the error of determining $d\pi/dP_w$ directly from equation (9) will not be serious.

The third source of error may be serious. The salt concentration in the soil solution of the different horizons of soil was determined at the termination of the experiment. It is quite possible that the picture of salt distribution among the horizons differed during the growing period from that found at the end of the experimental period. Also, some salt movement may take place within any given irrigation interval when the soil is being desiccated, but salt movement at this time would be more than counteracted by an irrigation. The foregoing thesis assumes uniform lateral distribution within a horizon, whereas a moderate degree of erratic variability is unquestionably involved. There will undoubtedly be a major differential between the salt concentration of the soil solution at the absorbing surface of the root and that a few millimeters away from an absorbing root, because of the ability of roots to absorb the water and exclude the salt. Accordingly the salt concentration at the absorbing surfaces of the roots will be higher than the average for the soil solution in a given small mass of soil.

It is difficult to evaluate fully these sources of error or ascertain the degree to which they may be self-compensating. It should be noted, however, that the total amount of solute in a container of soil is nearly constant over an experimental period. If this salt were in some manner maintained absolutely uniform in distribution throughout the soil solution, the value of Q throughout the whole soil mass of the example illustrated in figure 4, would be 1.33 atmospheres. For the variation in water content of the soil shown in figure 7, it may be shown that there would be 20.1 atmosphere-days for the irrigation interval or an average of 4.02 atmospheres per day. This value is nearly identical with that derived by taking into account the variation in salt content among horizons. This not only tends to discount the seriousness of the error due to vagaries in salt distribution, but it also raises the question of the need for taking into account any of the observed variability in salt distribution. It can be stated definitely that this

latter procedure is of especial necessity in cultures having high salt content in which sufficient salt accumulates in the lower horizon to prevent root penetration.

It must be conceded that the evaluation of the fourth group of errors pertaining to root behavior rests largely on theoretical grounds. The primary assumption made in the foregoing development was that the soil moisture stress over the various portions of the absorbing surface of the root system tends to approach uniformity. This assumption is fully in accordance with the second law of thermodynamics, in that it is assumed that the plant will not absorb water at a higher energy level if water is available at a lower energy level when the system is at equilibrium. But the tenability of this postulate is conditioned by the degree of constancy of the diffusion pressure deficit within the innumerable absorbing cells over the root system, and the degree to which equilibrium in this force is maintained among these cells. Furthermore, a growing plant is never in equilibrium with its environment. It is probable that the status of the two conditions pertaining to the absorbing forces of the roots deviates appreciably from the ideal. Variations in moisture stress over the root system may, to a slight degree, be concomitantly associated with variations in diffusion pressure deficit of the absorbing cells. Furthermore, this pressure deficit of the water in an absorbing cell is usually high enough that an appreciable variation in the pressure deficit of the external water is possible without exceeding that in the cell. Differences in magnitude of this diffusion pressure gradient would be reflected by variations in rate of absorption. In the final analysis, these variations in rate of absorption over the different parts of the roots system which were brought about by variations in the soil moisture stress would effectively tend to bring about uniformity in the external stress at a given time.

Finally, the validity of the foregoing thesis will be conditioned by the toxicity of the salines present in the soil solution, since the concept developed takes into account only the physical force exerted by the solutes. It is known that certain salines do have an inhibitive effect on plant growth over and above that which may be accounted for on the basis of osmotic forces. The magnitude of this effect is dependent on the kind of plant under consideration and the kind of ions present in the substrate. Magnesium salts, for example, are particularly toxic to most plants. However, the carefully controlled experiments of Hayward and Spurr (7), in which rate of water absorption was measured by potometers when corn roots were subjected to different salines, sucrose, and mannitol at isosmotic pressures, lend considerable support to the view that the major effect of the salts usually present in saline soil solutions is osmotic.

The discussion of the errors involved in making the present calculations does bring out certain inadequacies of the method. The latter may be partly ameliorated by refinements in technique. Consequently, the writer takes the position that this method of approach may prove helpful in more fully evaluating plant response in saline soils. For example, the growth response of guayule was found (18) to be closely related to the average integrated moisture stress as derived by the foregoing method for 14 different soil treatments varying in salt content and soil moisture regime. Even so, it is recognized that the average integrated moisture stress for the curve in figure 8 may not adequately express the physio-

logical effect of this extreme variation in moisture stress. It is conceivable that the high values for moisture stress present for a relatively brief time, as shown in figure 8, may have an exaggerated effect on plant response. Obviously, the relative effectiveness of various portions of the curve 8 upon plant response needs investigation.

SUMMARY

A mathematical method for evaluating the variations in energy content of the soil moisture being absorbed by a plant grown in a large container of saline soil is presented. The method takes into account variability in salt distribution within the soil, variations in moisture distribution of the soil at a given time, and variation in total moisture content with time. A discussion of the errors involved is also included.

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INFLUENCE OF FERTILIZERS ON THE YIELD AND COMPOSITION OF CERTAIN CROPS AND ON THE SOIL

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The object of this investigation was to learn the influence of barnyard manure and of commercial fertilizers on the yield and on the protein, phosphorus, sulfur, calcium, and magnesium contents of sugar beets, barley, wheat, and alfalfa. It differs from most experiments on this subject in that: (a) It was conducted on a soil high in dolomite, about 40 per cent of the soil being soluble in acid. The acid-soluble part consisted mainly of calcium and magnesium carbonates. (b) The crops were grown under irrigation on a porous soil with good drainage. (c) The soil carried large quantities of the essential elements, with the exception of nitrogen, which was low.

PLAN OF THE EXPERIMENT

The investigation was conducted on well-drained Millville loam with a sandy loam subsoil. The permanent water table is approximately 100 feet below the surface. The chemical and physical composition of the soil is similar to that of the soil on the adjoining Greenville Experimental Farm (3). It is rich in potassium and phosphorus, but comparatively low in nitrogen. Because of a high content of calcium and magnesium carbonate, it is slightly basic.

The soil lies in a productive area and can receive an optimum quantity of water; however, because of previous methods of farming without manure or fertilizers, the yields had been materially reduced. Commercial fertilizers were applied broadcast to each plot in the spring before the seedbed was prepared and were harrowed into the soil. The manure was applied every fall just before plowing. The fertilizer treatments of the plots were as follows:

O................. Check, no fertilizer
G................. Gypsum (plaster of paris), 500 pounds per acre
K................. Potassium chloride, 167 pounds per acre (61 per cent K_2O)
N................. Ammonium sulfate, 240 pounds per acre (20 per cent N)
N + K........... Ammonium sulfate, 240 pounds per acre (20 per cent N)
　　　　　　　　　Potassium chloride, 167 pounds per acre (61 per cent K_2O)
P................. Treble superphosphate, 350 pounds per acre (45 per cent P_2O_5)
P + K........... Treble superphosphate, 350 pounds per acre (45 per cent P_2O_5)
　　　　　　　　　Potassium chloride, 167 pounds per acre (61 per cent K_2O)
N + P........... Ammonium sulfate, 240 pounds per acre (20 per cent N)
　　　　　　　　　Treble superphosphate, 350 pounds per acre (45 per cent P_2O_5)
N + P + K...... Ammonium sulfate, 240 pounds per acre (20 per cent N)
　　　　　　　　　Treble superphosphate, 350 pounds per acre (45 per cent P_2O_5)
　　　　　　　　　Potassium chloride, 167 pounds per acre (61 per cent K_2O)
M*................ Manure, 10 tons per acre
M + PR.......... Manure, 10 tons per acre
　　　　　　　　　Raw rock phosphate, 3 tons per acre

M + PR + S...... Manure, 10 tons per acre
                 Raw rock phosphate, 3 tons per acre
                 Sulfur concentrate, 120 pounds per acre (81 per cent S)
M + P........... Manure, 10 tons per acre
                 Treble superphosphate, 350 pounds per acre (45 per cent P_2O_5)

* The manure contained approximately 3 pounds phosphorus, 14 pounds potassium, and 16 pounds nitrogen per ton.

The cropping system was a 6-year rotation, potatoes, sugar beets, barley, wheat, alfalfa, alfalfa, and repeat. Each crop appeared yearly; hence, the analyses represent samples for each year of the two rotations. Because of the uniformity of results, they were averaged. This gave an average of 12 analyses for each plant. Moreover, a number of fertilizers manifest no influence on the composition of the crop; hence the treatments are combined into the following six groups: (a) O, G, K; (b) N, N + K; (c) P, P + K; (d) N + P, N + P + K; (e) M, M + PR, M + PR + S, and (f) M + P. Analyses as reported, therefore, are from 24 to 36 crops and represent four to six separate analyses.

At harvesting, the various crops were sampled. Wheat and barley were stored for later analyses. Beets and potatoes were sampled, dried, and prepared for analysis as outlined elsewhere (4). Each sample was stored, and at the end of each rotation like samples were composited and analyzed according to A. O. A. C. methods (1).

RESULTS

Yield and composition of crops

Average yields and protein and phosphorus contents of potatoes are given in table 1. The largest increase in yield resulted from the manure and phosphorus. When used separately, both phosphorus and manure were effective. Ammonium sulfate and manure increased the protein content of the crop. This increase varied from 0.58 to 0.81 per cent. The increase from organic and commercial fertilizer is approximately the same. Manure increased the phosphorus content of the potatoes. In this regard, commercial fertilizers and manure are about equally effective. All samples were analyzed for calcium, magnesium, and sulfur. Neither the manure nor the commercial fertilizers influenced the quantity of these elements occurring in potatoes; hence, the calcium, magnesium, and sulfur contents of the crop are not given here.

The yield and the sucrose, purity, protein, and phosphorus contents of the sugar beets grown under varying manure and fertilizer treatment are given in table 2. Both phosphorus fertilizers and manure increased the yield but had little effect upon the sugar or purity content. Ammonium sulfate and manure increased the protein content of the crop. In this regard they are about equally efficient. Ammonium sulfate increased the protein content of the beets 0.32 per cent, whereas manure increased it 0.44 per cent. On an average, treble superphosphate increased the phosphorus content 0.054 per cent, whereas manure increased it 0.047 per cent. A combination of manure and treble superphosphate

increased the phosphorus 0.074 per cent. Both commercial fertilizers and manure were without effect on the calcium, sulfur, and magnesium contents.

Table 3 presents the yield and composition of the wheat grown with the various fertilizers. Manure was more effective than the commercial fertilizers in in-

TABLE 1

Yields and protein and phosphorus contents of potatoes grown with various fertilizers
Calculated to dry basis

TREATMENT	AVERAGE YIELD PER ACRE	PROTEIN	INCREASE IN PERCENTAGE OF PROTEIN DUE TO FERTILIZER	PHOSPHORUS	INCREASE IN PERCENTAGE OF PHOSPHORUS DUE TO FERTILIZER
	bu.	*per cent*		*per cent*	
O, G, K.......	280	9.50		.215	
N, N + K.....	297	10.31	.81	.215	.00
P, P + K.....	308	9.38	− .12	.269	.054
N + P, N + P + K........	353	10.25	.75	.272	.057
M, M + PR, M + PR + S.........	328	10.08	.58	.259	.044
M + P........	365	10.19	.69	.249	.034

TABLE 2

Yields and sucrose, purity, protein, and phosphorus contents of sugar beets grown with various fertilizers
Calculated to dry basis

TREATMENT	AVERAGE YIELD PER ACRE	SUCROSE CONTENT	PURITY BEET JUICE	PROTEIN	INCREASE IN PERCENTAGE OF PROTEIN DUE TO FERTILIZERS	PHOSPHORUS	INCREASE IN PERCENTAGE OF PHOSPHORUS DUE TO FERTILIZERS
	tons	*per cent*	*per cent*	*per cent*		*per cent*	
O, G, K.......	10.40	17.4	87.5	3.31		.060	
N, N + K.....	11.26	17.3	87.7	3.63	.32	.061	.001
P, P + K.....	15.53	18.1	88.8	3.31	.00	.109	.049
N + P, N + P + K........	17.40	18.2	88.7	3.47	.16	.119	.059
M, M + PR, M + PR + S............	17.84	17.5	87.8	3.81	.50	.107	.047
M + P........	19.47	17.8	88.2	3.75	.44	.134	.074

creasing the yield. Wheat grown with the ammonium sulfate contained an average of 0.67 per cent more protein than did wheat grown on check plots. The crop grown with manure contained 0.92 per cent more protein than did that grown on check plots. The wheat grown with treble superphosphate contained 0.082 per cent more phosphorus than did that grown on the check plot. On an average, manure increased the phosphorus content 0.053 per cent. Neither commer-

cial fertilizers nor manure had any effect upon the calcium, magnesium, and sulfur contents of the crop.

The yield and composition of barley grown with the various fertilizers are given in table 4. The commercial nitrogenous fertilizers and also the manure increased

TABLE 3

Yields and protein and phosphorus contents of wheat grown with various fertilizers

Calculated to dry basis

TREATMENT	AVERAGE YIELD PER ACRE	PROTEIN	INCREASE IN PERCENTAGE OF PROTEIN DUE TO FERTILIZER	PHOSPHORUS	INCREASE IN PERCENTAGE OF PHOSPHORUS DUE TO FERTILIZER
	bu.	*per cent*		*per cent*	
O, G, K.......	37.5	11.05		.390	
N, N + K.....	46.4	11.72	.67	.391	.001
P, P + K.....	39.9	10.80	−.15	.472	.082
N + P, N + P + K.......	51.9	11.02	−.03	.474	.084
M, M + PR, M + PR + S...........	52.5	11.97	.92	.443	.053
M + P........	53.8	11.80	.75	.459	.069

TABLE 4

Yields and protein and phosphorus contents of barley grown with various fertilizers

Calculated to dry basis

TREATMENT	AVERAGE YIELD PER ACRE	PROTEIN	INCREASE IN PERCENTAGE OF PROTEIN DUE TO FERTILIZER	PHOSPHORUS	INCREASE IN PERCENTAGE OF PHOSPHORUS DUE TO FERTILIZER
	bu.	*per cent*		*per cent*	
O, G, K.......	63.5	10.32		.320	
N, N + K.....	70.2	11.25	0.93	.317	−.003
P, P + K....	69.0	9.95	−0.37	.364	.044
N + P, N + P + K......	72.7	10.95	0.63	.370	.050
M, M + PR, M + PR + S..........	75.8	11.61	1.29	.418	.098
M + P........	75.0	11.15	0.83	.436	.116

the yield and protein content of the barley. The protein content was slightly greater where manure was used than where commercial fertilizers were used. The phosphorus fertilizers and the manure materially increased the yield and phosphorus content. All treatments were without effect on the calcium, magnesium, and sulfur contents.

The yields and the composition of first-crop alfalfa grown on untreated soil, and on soil treated with commercial fertilizers and with manure are given in table 5.

Commercial fertilizers were without effect upon the protein, calcium, and magnesium contents of alfalfa. Possibly the manure increased slightly the protein and sulfur contents, but it was without effect upon the calcium and magnesium. The phosphorus fertilizers, treble superphosphate, and manure were equally effective

TABLE 5

Yields and protein, phosphorus, and sulfur contents of first-crop alfalfa grown with various fertilizers

Calculated to dry basis

TREATMENT	AVERAGE YIELD PER ACRE	PROTEIN	INCREASE IN PERCENTAGE OF PROTEIN DUE TO FERTILIZER	PHOSPHORUS	INCREASE IN PERCENTAGE OF PHOSPHORUS DUE TO FERTILIZER	SULFUR	INCREASE IN PERCENTAGE OF SULFUR DUE TO FERTILIZER
	tons	*per cent*		*per cent*		*per cent*	
O, G, K.......	2.71	17.79		.193		.261	
N, N + K.....	2.63	17.72	− .07	.185	− .008	.343	.082
P, P + K...	3.09	17.97	.18	.279	.086	.289	.028
N + P, N + P + K......	3.22	18.13	.34	.280	.087	.322	.061
M, M + PR, M + PR + S...........	3.07	18.52	.73	.271	.078	.330	.069
M, M + P....	3.22	18.44	.65	.296	.103	.297	.036

TABLE 6

Yields and protein, phosphorus, and sulfur and contents second-crop alfalfa grown with various fertilizers

Calculated to dry basis

TREATMENT	AVERAGE YIELD PER ACRE	PROTEIN	INCREASE IN PERCENTAGE OF PROTEIN DUE TO FERTILIZER	PHOSPHORUS	INCREASE IN PERCENTAGE OF PHOSPHORUS DUE TO FERTILIZER	SULFUR	INCREASE IN PERCENTAGE OF SULFUR DUE TO FERTILIZER
	tons	*per cent*		*per cent*		*per cent*	
O, G, K.......	2.25	18.38		.219		.337	
N, N + K.....	2.24	18.65	.27	.208	− .011	.384	.047
P, P + K.....	2.52	18.85	.47	.272	.053	.330	− .007
N + P, N + P + K........	2.55	19.30	.92	.284	.065	.386	.049
M, M + PR, M + PR + S...........	2.53	19.04	.66	.268	.048	.368	.031
M, M + P....	2.51	18.69	.31	.296	.077	.396	.059

in increasing the yield and phosphorus content of the crop. Even alfalfa grown with manure and phosphate fertilizers would be classed as only medium-high in phosphorus, whereas alfalfa grown without a phosphate fertilizer is extremely low in phosphorus.

Results obtained on second-crop alfalfa (table 6) are practically the same as

those obtained on first-crop alfalfa. Ammonium sulfate had no effect on the protein content of the alfalfa, but the superphosphate and manure increased the yield and the protein and phosphorus contents. Ammonium sulfate increased slightly the sulfur content of the crop. All fertilizers, both commercial and organic, were without effect upon the calcium and magnesium contents of the alfalfa.

The composition of the variously produced third-crop alfalfa is given in table 7. Both the phosphate fertilizers and the manure increased the phosphorus content of the crop but were without effect on yield or on nitrogen, calcium, magnesium, or sulfur contents.

The composition of the combined first-, second-, and third-crop alfalfa is given in table 8. It is evident from the results reported that: (*a*) The composition of

TABLE 7

Yields and protein, phosphorus, and sulfur contents of third-crop alfalfa grown with various fertilizers

Calculated to dry basis

TREATMENT	AVERAGE YIELD PER ACRE	PROTEIN	INCREASE IN PERCENTAGE OF PROTEIN DUE TO FERTILIZER	PHOSPHORUS	INCREASE IN PERCENTAGE OF PHOSPHORUS DUE TO FERTILIZER	SULFUR	INCREASE IN PERCENTAGE OF SULFUR DUE TO FERTILIZER
	tons	*per cent*		*per cent*		*per cent*	
O, G, K.......	2.06	20.89		.239		.353	
N, N + K.....	1.97	21.03	.14	.240	.001	.415	.062
P, P + K.....	2.24	20.91	.02	.302	.063	.362	.009
N + P, N + P + K........	2.20	21.19	.30	.303	.064	.405	.052
M, M + PR, M + PR + S..........	2.28	20.65	− .24	.308	.069	.377	.024
M, M + P.....	2.33	20.81	− .08	.310	.071	.366	.013

first-, second-, and third-crop alfalfa produced on this soil differs. The protein, sulfur, and phosphorus contents of the first crop are lower than those of either the second or third crop, and the second crop is lower in these constituents than is the third crop. (*b*) Commercial fertilizer and barnyard manure are without effect upon the nitrogen content of alfalfa. Possibly these fertilizers increased the sulfur content of third-crop alfalfa. This must not be interpreted, however, as implying that sulfur-carrying fertilizers, when applied in other areas of the state, will increase the sulfur content of alfalfa. It may or may not, since this soil was found by Greaves and Gardner (2) to be very low in sulfur. The surprising thing is that sulfur does not have a more pronounced effect. Although only small quantities of sulfur are present in the soil, yet when supplemented with the sulfur of rain water, they are nearly sufficient to meet the sulfur requirements of alfalfa. (*c*) This soil, although well supplied with total phosphorus, does not carry enough available phosphorus to meet the needs of alfalfa. Alfalfa responds readily to

phosphorus fertilizer. This is manifest to a greater degree on the third crop than on the first or the second crop. (d) Alfalfa grown on this soil without phosphorus fertilizer is low in phosphorus, whereas similar alfalfa grown with phosphorus is fairly high.

Composition of soil

After the experiments had been continued for 12 years, the surface soil of the plots was sampled in the fall and analyzed for organic matter by the Schollenberger method (5); for available phosphorus with the improved molybdenum

TABLE 8

*Percentages of protein, sulfur, and phosphorus in first-, second-, and third-crop alfalfa grown on soil without and with fertilizer**

ALFALFA CROP	PROTEIN		PHOSPHORUS		SULFUR	
	Fertilizer A	Unfertilized	Fertilizer B	Unfertilized	Fertilizer C	Unfertilized
	per cent	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
First........	17.72	17.79	.279	.193	.343	.261
Second......	18.65	18.38	.272	.219	.384	.337
Third........	21.03	20.89	.302	.239	.415	.353

*Fertilizer A, manure or commercial fertilizer carrying nitrogen; fertilizer B, manure or commercial fertilizer carrying treble superphosphate; fertilizer C, commercial fertilizer carrying sulfates.

TABLE 9

Organic matter, available phosphorus and nitrates in fertilized plots at close of 12 years of cropping

TREATMENT	ORGANIC MATTER	PHOSPHORUS	NITRATES
	per cent	*p.p.m.*	*p.p.m.*
O, G, K.................	2.4	3	5.7
N, N + K...............	2.4	3	10.7
P, P + K................	2.4	32	5.0
N + P, N + P + K......	2.5	28	7.3
M, M + PR, M + PR + S.	2.9	13	11.4
M, M + P..............	3.0	55	12.8

reagents (6); and for nitrates, by the phenoldisulfonic acid method (1). The results are shown in table 9.

In 12 years' treatment the organic matter had been raised by the manure from 2.4 to 3 per cent but was not measurably affected by the other fertilizers. The available phosphorus had been increased from 3 to 32 p.p.m. by phosphorus fertilizer, to 13 p.p.m. by manure, and to 55 p.p.m. by manure and phosphorus fertilizers. The nitrate content had been raised from approximately 5 p.p.m. to approximately 10 p.p.m. by either nitrogen fertilizer or manure. The soil is so well buffered that none of the treatments exercised measurable influence upon the pH.

SUMMARY

Commercial fertilizers and manures carrying soluble nitrogen and phosphorus materially increased the yields of potatoes, sugar beets, wheat, and barley on a highly calcareous soil under irrigation. The percentages of phosphorus were increased in all crops, and nitrogen in all crops except alfalfa. Ammonium sulfate in the fertilizers slightly increased the sulfur content of the alfalfa. All fertilizers were without effect on the other constituents of the crops.

The composition of first-, second-, and third-crop alfalfa produced on this soil differs. The protein, sulfur, and phosphorus contents of first-crop alfalfa are lower than those of either second- or third-crop alfalfa, and second-crop alfalfa is lower in these constituents than is third-crop alfalfa. Alfalfa produced on this soil responds readily to phosphorus fertilizers, which bring about increased yields and higher percentages of phosphorus in the plants. Hence, although this soil is high in total phosphorus, it does not meet the growing needs of the alfalfa plants.

The following practical conclusions may be drawn from these studies: The nutritive value of alfalfa, with reference to protein and phosphorus content, is highest for the third crop and lowest for the first crop. Alfalfa grown on soil to which phosphorus fertilizers have been added would probably have a higher nutritive value than similar alfalfa grown on this soil without fertilizers.

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THE RÔLE OF CLAY MINERALS IN THE FORMATION OF SOIL STRUCTURE[1]

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Elucidation of some of the processes of soil structure formation was the objective of the work reported in this paper. It was attempted by comparing the relative binding action of montmorillonite and kaolinite, alone and with additions of sand, organic matter, $Ca(OH)_2$, and colloidal $Fe_2O_3 \cdot H_2O$.

Although flocculation of clay by H or Ca as compared to Na results in increased infiltration capacity of the clay and of clay membranes (9) and in the formation of flocks which are more stable in water (1), it has become apparent that the development of an ideal water-stable granular structure such as is found in the surface layers of natural soils cannot be the result of flocculation alone (3). Consequently the early emphasis on flocculation as the chief mechanism in soil aggregation has given way to the belief that cementation is responsible for the development of the comparatively large granules present in soils of good tilth and good structure (3). The bulk of the cementing material in soil aggregates is thought to be colloidal, and the mechanism of cementation is believed by some to depend on orientation of the colloidal particles (8, pp. 52–54; 14; 15; 18).

According to Russell (15), Sideri (16, 17) and Henin (8, pp. 52–54), orientation of clay particles takes place in a wet soil. As the soil dries, the cohesive forces between oriented clay particles increase. Because of the slow reversibility of well-oriented systems, subsequent oriented layers may be laid down and coat the original aggregate before its original components have dispersed, in this way adding to its size and stability. These assumptions supply a theoretical basis for the development of aggregates under the influence of cyclic wetting and drying.

EXPERIMENTAL PROCEDURE

The ability of kaolinitic and montmorillonitic clay to form water-stable aggregates when treated with various ingredients was tested by puddling the mixtures and exposing them to cyclic wetting and drying. The capacity of soils to develop granules after puddling when exposed to cyclic wetting and drying had been previously tested (13). A mixture of 1 part quartz sand to 9 parts clay was used throughout the experiment except in tests on the effect of varying amounts of sand and clay. Increments of ground alfalfa, colloidal hydrous ferric oxide, and $Ca(OH)_2$ were added to the clay and sand mixtures in triplicate sets. The amounts of materials used in the several treatments may be obtained from figures 2, 3, and 5.

The samples were worked thoroughly with a spatula after being brought to the moisture equivalent. The puddled mass was rolled into pellets and exposed to ten cycles of wetting and drying. After being wetted in a mist spray, the samples were left overnight in a moisture chamber. They were dried over a hot plate at an air temperature of 30° to 40° C., and after 1 minute of slaking in water they were wet-sieved through a 0.25-mm. screen in a sieving apparatus adjusted to thirty-eight 1½-inch strokes per minute (10).

The clays selected were a commercial sample of montmorillonite known as "vol-clay bentonite"—a Wyoming bentonite from the American Colloidal Company—and a sample of commercial kaolinite from the R. T. Vanderbilt Company, Bath, South Carolina. The exchange capacity of the kaolinite was 2.93 m.e. and that of the vol-clay bentonite, 89.8 m.e. per 100 gm. The clays and the sand were passed through a 0.25-mm. screen. The quartz sand was treated with
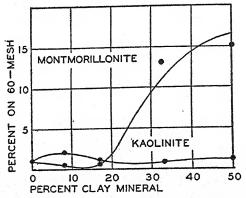
FIG. 1. EFFECT OF CLAY MINERALS ON THE FORMATION OF WATER-STABLE AGGREGATES IN SOIL

Soil from the B horizon of Tama silt loam sampled near Gladbrook, Iowa. As measured by resistance to wet-sieving.

H_2O_2 and HCl. The sample of soil from the B horizon of Tama silt loam was taken near Gladbrook, Iowa. According to a previous thermal analysis (14) the clay mineral content of this soil was mainly montmorillonitic with a small amount of kaolinitic clay.

RESULTS AND DISCUSSION

Effect of montmorillonite and kaolinite on aggregation of soil from the B horizon of Tama silt loam

The effect of increments of the two kinds of clay on the aggregation of soil from the B horizon of Tama silt loam is shown in figure 1. The total aggregation resulting from mixtures of kaolinite and soil is not appreciably different from that which developed in the untreated, puddled soil. Small additions of montmorillonite had little effect on the amount of material retained on the screen, but additions in excess of 20 per cent of the weight of the soil resulted in a substantial increase in material retained.

Apparently the crystals of montmorillonite did not function noticeably as a binding agent between discrete particles of the soil, but they did show strong attractions for one another. Consequently the binding action was not apparent until enough clay mineral had been added to ensure a continuous system of montmorillonite. With increases beyond this point, in proportion of montmorillonite in the mixture, the binding effect increased rapidly. When the concentration of clay mineral became so high that the properties of the mass became chiefly those of a montmorillonite system, further increments were less effective. The granules produced by mixtures of soil and montmorillonite seemed to possess a gel-like structure internally.
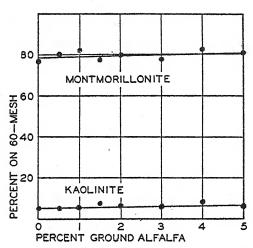
FIG. 2. EFFECT OF ORGANIC MATTER ON WATER-STABLE STRUCTURE OF MIXTURES OF KAOLINITE OR MONTMORILLONITE WITH SAND (9 PARTS CLAY TO 1 PART SAND)

As measured by resistance to wet-sieving.

Effect of organic matter on the water-stable structure of mixtures of montmorillonite or kaolinite with sand

From figure 2 it is apparent that organic residue left from the decomposition of alfalfa had little effect on the amount of material remaining on the screen. Apparently the characteristics of the systems containing 9 parts clay to 1 part sand were so dominated by the properties of the clays that any effects of the organic decomposition products were completely overshadowed, at least at the rates of organic matter used. Using mixtures of undecomposed, finely ground organic matter, sand, and montmorillonite, McHenry and Russell (10) found a reduction in the amount of material resistant to wet-sieving with additions of organic matter. They believed this was caused by the diluting action of the fragments of organic material.

In this experiment the mass of material remaining on the screens was not granular in the sense of water-stable granules of a sample of soil, but was gelatinous and globular, the globules hanging together in large clumps.

Effect of colloidal hydrous ferric oxide on water-stable structure of mixtures of kaolinite or montmorillonite with sand

Hydrous ferric oxide gel added to kaolinite did not increase the slight amount of water-stable structure which had developed in previously puddled pellets of that clay mineral and sand under the influence of cyclic wetting and drying. Little effect was noticed in the montmorillonite and sand until the amount of ferric oxide added was equivalent to 1.5 per cent of the dry weight of the sand and clay (fig. 3).

As in the case of the organic matter treatment, little structure seemed to develop in the kaolinite, whereas the montmorillonite series formed characteristic
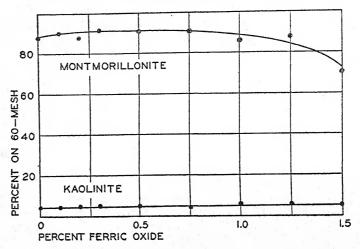
FIG. 3. EFFECT OF FERRIC OXIDE ON WATER-STABLE STRUCTURE OF MIXTURES OF KAOLINITE OR MONTMORILLONITE WITH SAND (9 PARTS CLAY TO 1 PART SAND)

As measured by resistance to wet-sieving.

gel-like masses on wetting. This fact seemed to justify the assumption that the forces contributing to the amount of material remaining on the screen where montmorillonite was used were those which contribute to gelation and which might or might not be those which produce water-stable granules in field soils.

Assuming that the globular mass remaining on the screens after wet-sieving is a true gel, the reduction in amount of gel by the 1.5 per cent rate of ferric oxide may be attributed to mutual coagulation of the negative montmorillonite gel by the positive ferric oxide gel as explained by Weiser (19).

Effect of different amounts of sand on mixtures of kaolinite and montmorillonite

As shown by the curves in figure 4, montmorillonite was more effective in building coherent globules, resistant to water slaking under the conditions of the experiment, than was kaolinite. Since Hauser (5) has pointed out that the capacity to produce a gel depends on the strength of the repelling forces and the

degree of hydration, the more highly charged and highly hydrated montmoril-
lonite would be expected to gel more readily than kaolinite.

The results of the test showed that a few quartz grains mixed in the clay gave
a more coherent mass than did the clay alone.   Since the increase in amount of
material resistant to wet-sieving was greater than could be explained on the basis
of sand immeshed in the clay gel, some advantage to the water-stability of the
system must have been contributed by the quartz particles.   With continued
dilution of the clay mixtures with sand, the trend was reversed and the systems
became progressively more subject to dissolution in water with increasing propor-
tions of sand.   Thus it would seem that although a few quartz particles aided the
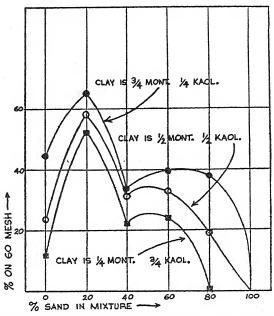
FIG. 4. EFFECT OF DIFFERENT AMOUNTS OF SAND ON MIXTURES OF MONTMORILLONITE AND
KAOLINITE

As measured by resistance to wet-sieving.

coherence and water-stability of the systems, excessive numbers weakened it
through excessive dilution of the clay, which because of its greater surface,
hydration, and activity would be the more active binding ingredient of the
mixtures.

A break in the continuity of the downward slope of the curves with increasing
amounts of sand indicates that the binding action at low rates of sand may be
different from those at high rates.   This discontinuity was also noticed by
McHenry and Russell (10) in studies of mixtures of sand and montmorillonite.
They thought the discontinuity might represent the region where clay particles
having satisfied all possible contact points on the sand grains had begun to ag-
glomerate among themselves.

*Effect of calcium on the water-stability of mixtures of sand with kaolinite
and montmorillonite*

Until Ca had been added in excess of the amount required to saturate the clay
it had no effect on the amount of kaolinite and sand resistant to wet-sieving after
ten cycles of wetting and drying (fig. 5).   Calcium in excess of this amount in-
creased the quantity of water-stable units apparently by cementation.   At the
higher rates of Ca the mixtures were quite granular, retaining their granular
appearance in water rather than forming a gel as did the montmorillonite mix-
tures.
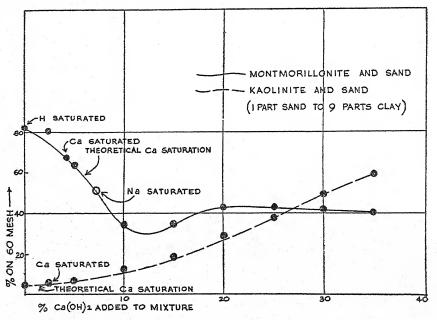
FIG. 5. EFFECT OF CALCIUM HYDROXIDE ON WATER-STABILITY OF AGGREGATES

As measured by resistance to wet-sieving.   Theoretical saturation represents the point
on the curve at which the added Ca is equivalent to the amount that would be held by the
mixture at saturation.

Upon drying, the mixtures of montmorillonite and sand formed characteris-
tically plastic, masses at the lower rates of Ca but as the amount of Ca was
increased there was a growing tendency toward granularity which was accom-
panied by a noticeable reduction in swelling.   When wet the mixtures became
masses of gel-like globules.   The individual globules were noticeably smaller and
more distinct with increasing amounts of Ca.

Apparently the gel formed from H-saturated montmorillonite was more resist-
ant to dispersion in water than was the Ca-gel, which in turn was more stable
than the Na-gel (fig. 5).   Reduction in the amount of material remaining on the
screen with additions of Ca(OH)$_2$ which supplied Ca above the amount needed
for saturation was probably due to dissolution of the gel through flocculation.

In observing the behavior of montmorillonite sols treated with increasing amounts of electrolyte, Hauser (5) noted that if only a slight excess of electrolyte was added beyond that needed to induce gelation, "ultra flocks" would form although the system was still a gel. Further additions of electrolyte resulted in microscopic, and finally, in macroscopic flocks. According to Baver's interpretation, viscosity curves for the Putnam colloid (1) reveal a gradual increase in flocculation of the clay as soon as additions of Ca exceed the saturation point.

The increase in amount of material remaining on the screen after the minimum had been reached, at about 12 per cent $Ca(OH)_2$ (fig. 5), may have been due to the cementing effect of the excessive amounts of lime. The failure of the curve to continue to climb with higher increments of lime, as did the curve for kaolinite, may have been the result of the shrinking and swelling of the montmorillonite, which would prevent the formation of large granules cemented by $CaCO_3$.

General discussion

Although it is apparent that we have been dealing with gels and flocks (6) rather than with granules of a shape and size found in soils of good structure, a consideration of recent ideas of soil structure formation (3, 7, 15) shows the possibility of a relationship between the amount of montmorillonite gel resistant to dispersion in water and the ability of the clay to act as a water-stable binding agent.

The development of the concept may be outlined thus: Orientation is essential to the cementing action of clay in binding soil aggregates; orientation takes place more readily if a soil dries with the clay in the state of a gel rather than flocculated. Conditions which permit orientation of the clay and at the same time result in a low rate of dispersion upon rewetting best favor water-stable aggregation. As a consequence those systems which form gels more stable in water may be the best cements for water-stable aggregates.

The detailed derivation of the concept is based on the studies of Russell (15) and Hauser (5, 6, 7).

Russell (15) reasoned that cations most effective in orienting water dipoles in linkages of clay particle-oriented water dipole-cation-oriented water dipole-clay particle, would be those cations of least ionic diameter because they would have the greatest mean surface density of charge. Hence for cations of the same charge, the capacity to orient clay particles and produce hard crumbs on desiccation increases as the ionic radii decrease. Because it also follows, however, that the affinity of the ions for water as indicated by extent of hydration (4) increases in the same way, with the exception of H, the smaller cations, except H, produce less stable crumbs. Water-stable crumb formation therefore depends on the presence of linkages which are strong enough to orient the particles but which are not readily destroyed on rewetting. Since the orientation of the smaller, discrete clay particles would occur more easily than orientation of larger, comparatively electrically neutral flocks, a dispersed clay should be more readily oriented on drying than is a flocculated clay.

Hauser (7) has shown that the alignment of montmorillonite particles into

interlacing filaments of continuous threadlike aggregations of highly anisotropic shape, takes place during the drying of the gel. If flocculation was carried out into the visible range before drying, only small water-stable flocs were formed instead of a continuous oriented system. The inability of flocs to form coherent structures was attributed to the fact that the flocs were already fully neutralized prior to the orienting processes which develop during drying.

Hauser (5) was able to demonstrate that as a montmorillonite sol changed to a gel on the addition of an electrolyte, the individual particles of clay assumed fixed positions, each particle appearing as a discrete unit completely separated from any others. He believed these gels were formed by particles taking up equilibrium positions in relation to one another as a result of the balancing of forces of attraction and those of repulsion. The attractive forces he considered to be constant for particles of equal size and density. The repulsive forces would vary with the electric charge of the particle, the composition and nature of the ion arrangement in the dispersion medium, and the lyosorption or solvation. Hence, other things being equal, homoionic clays saturated with the more highly hydrated cations should form gels which would develop more readily but which would be more easily dispersed on dilution.

Thus the ideas of Russell (15) and of Hauser (5, 6, 7) are in agreement in that the more easily hydrated cations can be expected to be more effective in setting the stage for the orientation of clay particles. Yet these same cations may be less effective in producing water-stable granulation in soils because of their strong attractions for water which cause them to act as dispersing agents when water is added.

If gelation does set the stage for orientation of the particles of clay and if orientation is a step in the process of soil structure formation, then it does seem logical that the more water-resistant gels would result in cementing materials which were also more water-resistant. Thus a H-clay would result in a more permanent aggregate than would a Ca-clay, which in turn would form a more stable aggregate than would a Na-clay, a conclusion which is in line with the observed conditions in natural soils.

The superiority of divalent cations to monovalent cations in their effects on physical properties of soils is a well-established fact. The one exception is H which has at least as good influence on soil structure as does Ca. The subject has been thoroughly reviewed by Baver (3), who pointed out that H was more effective in flocculating clay than was Ca, that H-clays were more permeable than Ca-clays (9), and that there was no significant correlation between the amounts of exchangeable Ca and granulation in 77 different soils. Baver (3) also drew attention to the fact that H and Ca both affected organic colloids in ways that would make those colloids more effective in producing water-stable aggregates. With Hall (2), he showed that dried Ca-humus was more reversible than dried H-humus, which was in line with Myers's (12) discovery that aggregates bound by H-humates were more stable than those by Ca-humates.

Thus for the cations used in this study the relative effectiveness in producing water-stable granules and good physical conditions in soils could be expected to

be in the order H, Ca, Na, which is the reverse order of their effect on the swelling of clays (11). It is, however, the same order as the relative effectiveness of the ions in flocculating clays (3), as their ability to increase the permeability of clays and of clay membranes (9) and as their capacity to form water-stable humus (2) and water-stable aggregates of humates (12). According to the results of this experiment, it is also the same order as their relative effectiveness in increasing the resistance of montmorillonite gels to dispersion in water.

SUMMARY AND CONCLUSIONS

An attempt was made to measure the relative capacity of kaolinite and montmorillonite to form water-stable aggregates under the influence of cyclic wetting and drying. The kaolinite was found to be very inert as a binding agent, having little effect on aggregation. Montmorillonite formed gel-like globules which varied in resistance to dispersion in water according to the conditions of the experiment. The difference in behavior of the two clays was attributed to the greater surface, hydration, and charge of the montmorillonite in comparison with the kaolinite.

Kaolinite had no apparent effect on the state of aggregation that developed in a puddled Tama soil. Montmorillonite markedly increased the amount of material resistant to wet-sieving but only when enough of the clay had been added to give it a dominating role in the mixture.

When mixtures of sand and clay treated with different amounts of ground alfalfa were incubated for 1 month before puddling and then exposed to cyclic wetting and drying, the alfalfa had no effect on the amount of material resistant to dispersion in water. This was true for both kaolinite and montmorillonite.

Hydrous ferric oxide had no effect on the aggregation of kaolinite and sand. However, when oxide equivalent to 1.5 per cent of the dry weight of the mixture was added, it decreased the amount of montmorillonite gel remaining on the screens, possibly through the mechanism of mutual flocculation.

Small amounts of sand added to mixtures of kaolinite and montmorillonite increased the resistance of the mixtures to dispersion in water. Larger amounts of sand had a reverse effect.

On the basis of the work of Russell and of Hauser and Lebeau, it is postulated that, to act as a cementing agent in the development of granules such as are found in field soils, clay must dry from a gel rather than a flocculated state. Cements formed from clays drying out of gels where the absorbed cations are less hydrated should be more water-stable than those from gels where the cations are more highly hydrated. Gel-like globules of mixtures of sand and homoionic montmorillonite were found to be more water-stable, in the order of H-clay, Ca-clay, Na-clay.

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DYNAMICS OF WIND EROSION: V. CUMULATIVE INTENSITY OF SOIL DRIFTING ACROSS ERODING FIELDS[1]

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In an earlier study (2) it was found that the rate of soil flow began with zero at the windward edge of an eroding field and in the majority of cases increased steadily all the way up to the leeward side. This rate of increase was not always uniform or the same in every case.

The causes of the cumulative rate of soil movement and of the variations in the rate of soil flow in different fields were not thoroughly understood at the time of the study. A further study was therefore undertaken, and the data obtained and presented herewith are believed to give the answers to these questions. Information is also given on the relationship of this cumulative intensity of soil movement to the strip-farming method of soil-drifting control.

EXPERIMENTAT PROCEDURE

Measurements of the rate of soil flow at different positions across eroding fields situated on several major soil types were made with Bagnold sandcatchers (1) during the years 1938 to 1944. The catchers were suitable only for measuring the rate of flow in saltation and surface creep, as fine dust carried in suspension was not trapped. As the proportion of the various types of flow remains more or less the same, however, for a given set of soil conditions, irrespective of wind velocity (4), the rate of total soil flow may be assumed to vary more or less directly with the rate of flow in saltation and surface creep.

It was extremely difficult to make the measurements over a much greater distance than 500 yards, partly because of the inaccuracy involved in setting the individual catchers at too great intervals of time and partly because of the inevitable variations in topographic and surface conditions within the area of the experiment. Despite these interfering factors, a general upward trend in the rate of soil movement toward the leeward side of eroding fields was plainly indicated in every case.

RESULTS

The rate of increase of erosion with distance to leeward across eroding fields varied widely on different soil types, as indicated by typical data in figure 1. The rate of increase on Haverhill loam and clay loam soils was approximately the same across the whole length of the field, but on highly calcareous Sceptre heavy clay the rate of increase was very rapid at first but became progressively

less rapid the greater the distance away from the windward edge. On all of these soil types no difficulty was experienced in locating eroding fields of 350 or more yards in width. The longest distance to leeward in every case in figure 1 designates the leeward edge of that particular field.

Because of the extreme erosiveness of Hatton fine sandy loam, eroding fields on this soil type were never found to exceed 200 yards in width. Typical results on rates of soil movement on this soil type are also given in figure 1. In this case, the rate of increase of soil flow was very rapid throughout the whole width of the field, although it began to diminish slightly after a distance of 100 yards was reached. Had the field been larger, it appears that the rate of soil flow along the lateral distance away from the windward edge would have followed more or less
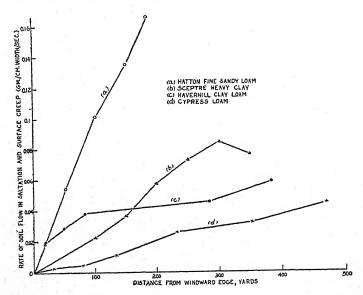
FIG. 1. TYPICAL VARIATIONS IN THE RATE OF SOIL MOVEMENT ACROSS WIND-ERODED FIELDS ON DIFFERENT SOIL TYPES

the same general trend as that on Sceptre heavy clay, but on a much greater scale.

At a distance of 100 yards, which represents the most general width of fallow strip used in the strip-farming system generally adopted for wind-erosion control, the intensity of erosion over Haverhill loam and clay loam soils was 18.7 and 26.7 per cent of the maximum intensity found near the leeward side of the exposed field; but over Sceptre heavy clay and Hatton fine sandy loam it was 63.0 and 63.1 per cent at the same distance to leeward. These results appear to have a direct bearing on the relative usefulness of strip farming on different soil types. Had the fields shown in figure 1 been divided into alternating fallow and stubble strips 100 yards wide, the maximum rate of soil movement would have been 18.7, 26.7, 63.0, and 63.1 per cent respectively of the rate that was found on the leeward side. It is therefore evident that strip farming is much less effective on

fine sandy loam and heavy clay soils than on loam and clay loam soils. This conclusion is substantiated by general experience.

Dry-sieving analyses of the soil fractions carried by wind across drifting fields in some instances showed a marked degree of sorting of the different sizes of particles. The coarser fractions moved more slowly than the finer ones, and this resulted in considerable segregation of sizes of grains, the coarser tending to remain nearer the windward edge of the field and the finer to accumulate nearer the leeward. This situation is plainly indicated by data in table 1 obtained on the day (April 15) of the first erosive wind of 1941. Drifting began about 9.30

TABLE 1

Size distribution of soil fractions carried by wind across a bare field of Haverhill clay loam

DISTANCE FROM WINDWARD EDGE OF FIELD*	SIZE DISTRIBUTION OF MOVING PARTICLES				
	>0.83 mm.	0.83–0.42 mm.	0.42–0.25 mm.	0.25–0.1 mm.	< 0.1 mm.
yds.	per cent	per cent	per cent	per cent	per cent
100	1.9	27.0	30.0	22.8	18.3
150	1.2	23.6	25.4	27.9	21.7
200	0.5	13.2	23.4	36.0	26.9
250	0.4	4.1	20.6	46.7	28.2
300	0.4	5.4	19.8	40.4	34.0
350	0.3	5.7	17.6	35.4	41.0

* Distance measured along the direction of the wind, the last location being near the leeward edge of the field.

TABLE 2

Variation in the dry clod structure of soil across a wind-eroded summer-fallow field

DISTANCE FROM THE WINDWARD EDGE	SIZE DISTRIBUTION OF DRY SOIL FRACTIONS TO 2-INCH DEPTH						
	> 38 mm.	38–12.7 mm.	12.7–6.4 mm.	6.4–2.0 mm.	2.0–0.83 mm.	0.83–0.42 mm.	< 0.42 mm.
yds.	per cent	per cent	per cent	per cent	per cent	per cent	per cent
16.7	7.4	20.4	6.4	4.1	2.9	5.8	53.0
100.0	0	10.3	8.3	4.9	3.4	7.0	66.1
183.3	0	7.6	7.2	5.1	3.6	12.3	64.2

a.m., and measurements were made between 10.30 and 11.00 a.m. By that time a considerable amount of sorting of the different sizes of soil particles had already taken place across what originally appeared to be a very uniform field. This sorting action was believed to be partly responsible for the variation in the rate of soil movement across eroding fields.

Many cases were found, however, which showed that the rate of soil flow varied irrespective of whether the soil material was sorted or was merely in the initial stage of being sorted into the various grades across the field. As erosive winds did not continue from any one direction, a change in wind direction altered the original trend in the grading process and sometimes even carried some of the soil back to near its original location. Yet a steady increase in the rate of soil movement with distance away from the windward edge was found in almost

every case. It was evident that the grading of soil material by the wind was only slightly, if at all, responsible for the variation in the rate of soil flow, but that some other factors were involved.

The next problem was to determine the quantity of erosive grains at different positions across the fields. Dry-sieving analyses of soils to the depth of 2 inches were made, and these showed in the majority of cases a tendency of erosive material (<0.83 mm.) to accumulate toward the leeward side of fields (table 2). This accumulation, increasing in the direction parallel to the direction of the wind, appeared to be responsible for the steadily increasing quantity of moving soil. A reversal in wind direction produced a corresponding accumulation of drift in the opposite direction. Immediately after the reversal of the wind, a more or less constant rate of flow throughout most of the field was observed, but not for very long. In a few hours the same situation with regard to an increasing rate of flow was established, but in a direction parallel to the new direction of the wind.

This increasing rate of flow across eroding fields appeared to be due mainly to the fact that cultivated soils are composed of a mixture of erosive and nonerosive fractions. As the ratio of erosive to nonerosive fractions at the surface became greater to leeward, because of the sorting action of the wind, the rate of flow increased in like proportion, until for material composed only of erosive fractions the rate of flow was the maximum that a wind of a given velocity could carry. In most cases this maximum rate was not reached in a distance of 500 yards.

On the other hand, the smaller the proportion of erosive fractions located on the surface of the ground, the lower was the rate of flow, and where the rate of removal of these fractions was greater than the rate of deposition of soil brought in from the windward direction, the rate of flow declined proportionately. On the extreme windward side of the fields, only removal was taking place, and it was not long before all of the erosive fractions were moved to leeward and the soil surface became completely stabilized by fractions too coarse to be moved by the wind. On a fairly smooth surface of loam soil 1 hour of continuous erosive wind coming from one direction was required to stabilize a distance of 20 feet from the windward edge. Assuming the same rate to continue across the whole width of the field, at least 120 hours of continuous exposure to erosive wind blowing from one direction would be required to stabilize a ½-mile length of fairly smooth fallow land, but the time required would easily be doubled for a ridged surface. Such length of time for erosive wind to blow continuously from one direction has not, so far as is known, been recorded on this continent.

The soil surface was observed to become progressively smoother with continued exposure to erosive wind. This process was apparently due to accumulation of fine fractions between and over coarse nonerosive granules and clods and to disintegration of surface projections by impacts of moving grains. The disintegration, or abrasion, of indurated soil materials was more intense the farther the distance to leeward, where a greater quantity of moving soil particles was found. That is, the greater the rate of soil movement, the greater was the rate

of disintegration of nonerosive to erosive fractions which, in turn, abraded more nonerosive clods and surface crust. This cumulative intensity of abrasion was particularly marked on soft, loosely held soil material, such as Hatton fine sandy loam.

The data in table 2 show a gradual disappearance of large clods to leeward of an eroding field. The disappearance of clods from the first 2 inches of surface soil is due to the increased rate of abrasion and the partial burial of the clods by erosive fractions that were blown in from the windward direction. Both of these processes tended to smooth out the surface, and as shown previously (3), this change alone causes a substantial increase in the rate of soil flow.

DISCUSSION

The gradual increase in the rate of soil movement toward the leeward side of wind-eroded fields is apparently caused by three main factors. One is the progressive accumulation of erosive particles toward the leeward side of fields. The steadily increasing accumulation of the erosive fractions on the surface of the ground produces a condition that is increasingly more susceptible to erosion by wind, until for material composed only of erosive fractions the susceptibility, as measured by the rate of soil flow, is the highest possible for the particular soil type and wind velocity.

The second factor is the cumulative degree of abrasion resulting from impacts of grains in saltation. As the concentration of erosive grains increases gradually to leeward, so likewise is the rate of breakdown of soil clods and surface crust to fractions which are fine enough to abrade and erode more soil clods and surface crust on their journey with the wind.

The third factor is the gradual decrease of surface roughness toward the leeward part of the fields. The decrease in surface roughness with distance to leeward is produced partly by the steadily increasing abrasion of surface projections and partly by the ever-increasing accumulation of erosive fractions between and over the soil clods and other similar surface obstructions.

The data further indicate that there is a marked degree of sorting of the different sizes of soil grains by the wind. This phenomenon acting on the soil throughout the course of many years causes it to become progressively coarser in texture, much of the silt and clay particles being carried away, leaving sand and gravel behind. The separation and removal of fine dust by the wind can be detected even by casual observation.

Once the main reasons for the changes in the intensity of erosion at different lateral positions across eroding fields have been determined, it becomes relatively simple to interpret the causes for the differences occurring in these changes on the different soil types that have been investigated.

The data indicate that there is a rapid increase in intensity of soil drifting near the windward edge of a field of highly calcareous heavy clay soil followed by a nearly constant rate of flow along the remaining part of the field, as compared to a relatively uniform rate of increase of erosion across the whole length of the

field on loam or clay loam soil.   These differences are apparently due to three reasons.

First, calcareous clay soils are highly granulated, containing a relatively thick layer of erosive particles at the surface which will not become stabilized even after rather long exposure to the wind.   Except on the extreme windward side, the rate of soil flow is, therefore, more or less uniform across the field.   The medium-textured soils have fewer erosive particles on the surface, and consequently there is a tendency for complete removal of erosive fractions from the windward side, the shorter the distance to the windward side the greater the percentage of removal and the lower the rate of flow.   On medium-textured soils there is therefore a gradual accumulation of erosive particles toward the leeward side of a field, and it is this type of accumulation that is directly associated with the intensity of soil flow.

In the second place, the differences are due to the fact that clay soils are virtually nonabrasive, whereas the coarser-textured soils are much more readily abraded (5).   As already pointed out, the more susceptible the soil is to abrasion, the greater is the rate of increase of erosion as one travels across the field with the wind.

Finally, because of the rapid rate of granulation under ordinary weather conditions, calcareous clay soils usually have a very smooth surface, particularly in the spring when erosive winds are the strongest.   Medium-textured soils are usually rougher and serve to trap greater quantities of erosive particles, thus increasing the distance at which complete smoothing out of the surface and consequent maximum intensity of erosion is established.

The variations in the rate of soil flow across fields of fine sandy loam appear to follow the same general trend as for calcareous clay soils, but for entirely different reasons.   The rapid increase in the rate of soil flow near the windward edge of this soil class is due primarily to loosely cemented clods and surface crust, which are very readily disintegrated by impacts of eroding grains.   This condition results in a particularly rapid rate of increase of erosion which in a relatively short distance often approaches an intensity equal to that of dune sand.

SUMMARY

The steadily increasing amounts of erosive particles, the cumulative degree of abrasion, and the gradual decrease in surface roughness along the direction of the wind were found to be the main causes for the gradual increase in the rate of soil movement with distance away from the windward edge of eroding fields.

The data indicate that there was a considerable amount of sorting of the different sizes of soil particles by the wind, the coarser particles tending to remain nearer the windward edge, the finer tending to accumulate nearer the leeward.

The causes for the variations in the rate of increase of soil flow on different soil types and the relationship between these variations and the strip-farming method of soil-drifting control have been presented.

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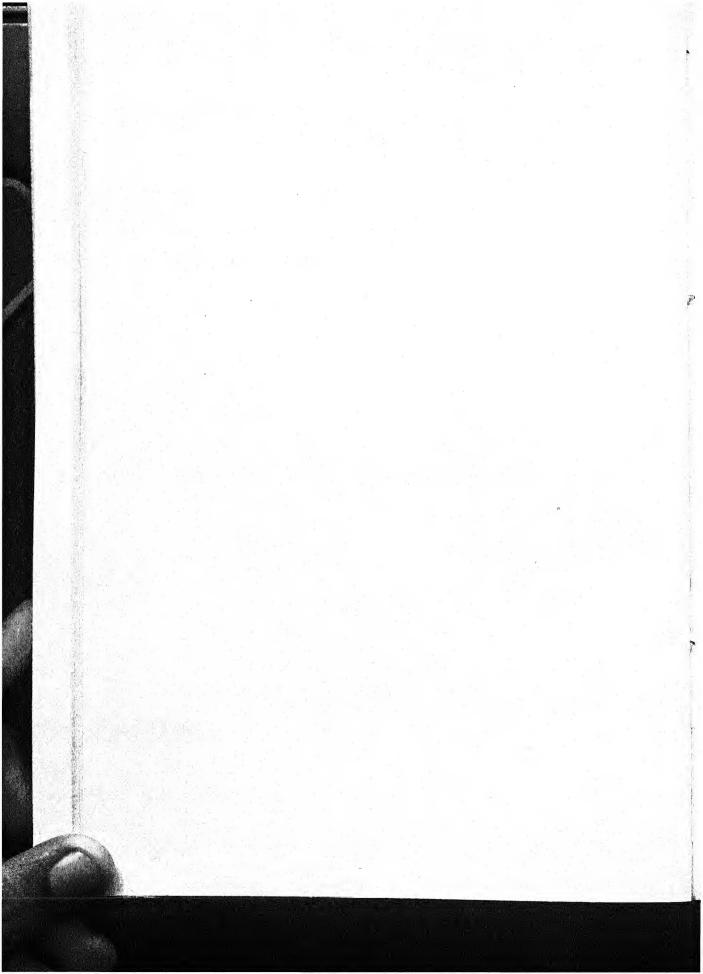
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PLANT NUTRITION AND THE HYDROGEN ION: V. RELATIVE EFFECTIVENESS OF COARSELY GROUND AND FINELY PULVERIZED LIMESTONE[1]

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The fact that limestone is used on humid soils more particularly to supply calcium and magnesium as plant nutrients than to supply carbonate for the reduction of soil acidity gives new significance to the amounts of limestone applied per acre and to its fineness of grinding. It prompts consideration of the mechanisms by which fragments of a natural, insoluble, secondary mineral or rock, mixed through the soil, may serve in nourishing plants. The corn yields produced in some trials where 10- and 100-mesh limestones were applied at different rates to sweet clover grown as green manure ahead of corn in a corn-oats rotation suggested the presentation of some probable mechanisms by which such mineral particles serve. Furthermore, these trials may be the means by which some theoretical soil-plant interrelationships can be shown.

PLAN OF LIMESTONE TRIALS

In two series of 16 plots each, both corn and oats were grown annually in a 2-year rotation from 1936 through 1944. On seven of the plots in each series, calcium only was applied.

Two of the calcium-treated plots received 10-mesh limestone. This was a high-grade calcium limestone, all of which passed through a 10-mesh screen. As a "mill-run" product it had the usual average distribution on the test screens of different finenesses. About 25 per cent passed through a 100-mesh screen. On one of the plots the limestone was drilled at the rate of 300 pounds per acre at each seeding of oats and sweet clover. Thus, four applications were made during the experiment. On the other plot, the limestone was broadcast at the rate of 2 tons per acre when the trials were started.

On three of the calcium-treated plots a calcium limestone of 100-mesh fineness was used. On one plot the stone was drilled at 300 pounds per acre with each seeding of the oats and sweet clover. To another plot, 600 pounds per acre was applied similarly. The third plot received only one application—2 tons broadcast in 1936.

The remainder of the calcium-treated plots were given calcium in the more readily soluble forms. On one, calcium sulfate was drilled with the seeding of oats and sweet clover, and on the other, calcium chloride was used. Both were

applied at rates supplying the calcium at the equivalent of that in the 300 pounds of limestone.

The sweet clover was seeded with the oats and grown as a stubble crop and green manure to be turned under the following spring ahead of the corn planting. The effects of the calcium as fertilizer treatments were measured by the corn yields.

The soil was Putnam silt loam, which had a pH of 5.5 as a general average. Without soil treatment, sweet clover failed to grow.

The first year, because of drought, no corn crop was obtained. In this report, only the last three corn crops on each of the two-plot series, A East and A West,

TABLE 1

Yields of corn in a 2-year rotation of corn and oats-sweet clover where different amounts of limestone of different degrees of fineness were used to establish the sweet clover

Yields in bushels per acre

PLOT NO.*	TREATMENT	YIELDS OF CORN						Mean (8 crops)
		Series A East			Series A West			
		1940	1942	1944	1939	1941	1943	
1	100-mesh limestone, 300 pounds per acre	36.5	32.6	30.8	26.6	49.8	35.6	33.6
8	10-mesh "mill-run" limestone, 300 pounds per acre	53.0	51.0	36.7	34.4	44.6	42.8	41.8
2	100-mesh limestone, 600 pounds per acre	42.9	39.7	33.7	37.4	63.7	41.6	39.7
9	Gypsum, Ca-equivalent of 300 pounds limestone	42.7	46.5	29.7	32.2	39.6	40.1	36.3
11	Calcium chloride, Ca-equivalent of 300 pounds limestone	42.5	46.1	33.6	30.4	39.2	39.5	36.5
14	10-mesh "mill-run" limestone, 2 tons per acre	67.8	72.5	44.8	41.1	61.6	51.7	50.3
16	100-mesh limestone, 2 tons per acre	58.3	54.4	38.9	47.6	63.2	50.6	46.4

* For plots 1, 2, 9, and 11, the years 1939 and 1940 represent two lime treatments ahead of the corn; 1941 and 1942 represent three; and 1943 and 1944 represent four. Plots 14 and 16 had one application of limestone in 1936.

The mean yield of 15 crops from the check plots in duplicate was 34.1 bushels per acre.

are considered individually, although all eight of the crops are included in the average figures presented in table 1.

RESULTS

The corn yields showed very significant increases from the drilling of only 300 pounds of 10-mesh limestone per acre. These yields were decidedly higher than those obtained by drilling the same amount of 100-mesh limestone. In fact, for four of the last six years of the trial, reported in table 1, the corn yields from the 300 pounds of drilled 10-mesh stone were higher than those from 600 pounds of 100-mesh stone applied in the same manner. The corn yields, as averaged for the 8 years, were higher for the drilling of the 300 pounds of 10-mesh limestone than for the use of the equivalent of this amount of calcium as gypsum or chloride, or for the drilling of 600 pounds of 100-mesh limestone. Higher corn

yields than those from the 300 pounds of 10-mesh were obtained only from the heavier, broadcast applications of 2 tons per acre.

The 10-mesh limestone was also superior to the 100-mesh stone when both were broadcast once in the 8 years at the rate of 2 tons per acre. This was true for four of the six annual comparisons given in the table. For the 8-crop average, the difference amounted to almost 4 bushels per year in favor of the coarse stone.

The corn yields, as an average, from three additional plots all given 2 tons of 100-mesh limestone in combination with phosphorus on one, with potassium on the second, and with both phosphorus and potassium on the third, were less than those from plots on which 2 tons of 10-mesh limestone were used without other fertilizers.

DISCUSSION

When the average yields for the eight crops are considered, there is evidence that the calcium in either of the readily soluble forms of sulfate or chloride had beneficial fertilizer effects. When an application as small as 300 pounds per acre of 10-mesh mill-run limestone is as beneficial as is indicated by these results, its effects can scarcely be ascribed to the reduction of soil acidity. The effects of such a small application must put the limestone into the category of a plant nutrient or fertilizer.

More significant, however, than its service in supplying calcium, is the fact that this calcium fertilizer applied in the form of coarser particles of rock fragments produced a greater crop yield than it did when applied as the more finely ground 100-mesh stone or as the more soluble salts. That small amounts of a rock which is only slowly soluble should be so much more effective an aid to the crops than were the finely pulverized and soluble forms is the feature that invites careful thought.

This fact suggests that a few foci of less soluble limestone in the soil volume reacting slowly with the clay are more effective in providing the plant with calcium than are the more soluble forms reacting rapidly with the clay. It suggests a mechanism in which there are, first, a movement of nutrients from the mineral and rock fragments to the acid clay by an exchange for the hydrogen, and, second, further movement of these nutrients from the clay to the plant root. In the opposite direction, from the root to the clay and to the mineral fragments, is moving the hydrogen originating in the root respiration that gives off carbon dioxide or other acidic compounds, by which, in the final analysis, the minerals and rocks are weathered. This slower delivery of nutrients from the breakdown of larger particles of limestone may well be more nearly the optimum rate for the delivery of calcium to the sweet clover than is the saturation of the clay by quickly acting calcium salts and rapidly dissolving 100-mesh limestone.

According to this concept, the limestone serves to nourish the plant with calcium more effectively when granules or particles in silt and sand size are distributed through the acid soil as focal mineral sources than when the calcium supply is only that adsorbed on the clay. The better crop of sweet clover during the first year of its biennial life and its better survival through winter into the second

year, where the 10-mesh limestone was used, suggest that this slower rate of calcium delivery over a longer period was more effective in providing this nutrient to keep the sweet clover growing than were the 100-mesh particles of stone or the calcium salts which delivered exchangeable calcium in the same or larger amounts promptly on application to the soil.

This suggests that small amounts of limestone and possibly other fertilizers, whether natural minerals or soluble salts, may be most efficient when these are of granular sizes distributed through the acid soil. Since 2 tons of 10-mesh mill-run stone was also more effective than an equal quantity of 100-mesh stone, it may be helpful, in getting a better concept, to note the number of particles of different sizes present per unit soil volume when 1 ton of limestone is distributed uniformly through the surface soil. Such data are assembled in table 2. From this it is evident that the coarser materials give only a few foci of calcium saturation in a given volume of acid soil. It also points out that it must be in part the movement

TABLE 2

Number of particles of limestone of constant sizes and their surface areas exposed when a ton is uniformly distributed per acre 7 inches

DIAMETER OF PARTICLES*	inches cm.	1/10 .254	1/20 .127	1/40 .0635	1/60 .0421	1/80 .03175	1/100 .0254
Surface per particle........ sq. in.		.031416	.007854	.001963	.0008727	.000490	.00031416
Weight per particle........ gm.		.0231	.0002895	.0003619	.0001054	.00004524	.0000231
Number of particles per cubic inch of soil............................		1	7	57	196	456	894
Particle surface per cubic inch of soil..................... sq. in.		.03141	.05497	.11192	.17104	.22344	.28085

* It is assumed that all particles within a particular diameter are spheres of one diameter.

of the roots by growth through the soil, and not wholly the diffusion of the calcium, that makes the root contacts with these more nearly calcium-saturated areas a means of providing the crop amply with calcium.

From studies of plant root-clay interactions (1), of clay behavior in its contact with mineral fragments of particular size (4), and of reactions of plant root-mineral contacts (5), it is becoming increasingly evident that soil acidity on the clay fraction is an essential phase in nutrient mobilization (3). It is also evident that complete neutralization of the soil acidity leads to nutritional troubles in plants. Iron immobilization with its consequent chlorosis, lowered availability of soil phosphorus, and deficiencies of manganese for plants are some of the unfavorable conditions brought about when the soil is made neutral (2, 7).

The significance of soil acidity as a nutrient mobilizer in ecology may be realized when it is recalled that most vegetation is naturally placed on acid soils and that little is on neutral and alkaline soils. Acidity in the soil is one of the necessary conditions by which nutrients are weathered out of the reserve minerals, passed to and stored on the colloidal clay, and held there in exchangeable forms

from which the advancing root can rapidly take its needed supply during its short growing season (fig. 1).

This concept of the mobilization of the plant's nourishment from mineral nutrient reserves in rock fragments simplifies the ecological array of different plants in relation to soil development. On the soils under low rainfall and scant soil development, which are mainly rocks and rock fragments with little clay saturated with cations other than hydrogen, the annual quantity of vegetative production is low. Woody shrubs or trees occur on such soils.

Soils with the original rock reserves broken down to sand and silt sizes, but not highly leached, have larger amounts of clay. This is not so highly saturated with
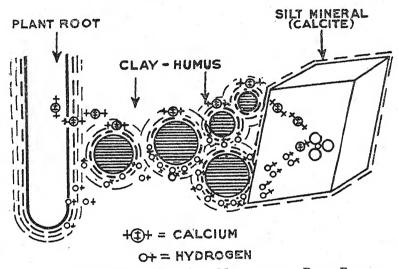
FIG. 1. DIAGRAM OF THE SUGGESTED MECHANISMS OF PLANT FEEDING

Hydrogen, as acidity, in the soil seems as essential as the nutrient cations if plant nutrition demands the weathering out of the nutrient mineral reserves through microbial activities and root respiration. The hydrogen potential grades through the colloids from the root to the mineral, while the fertility potential grades in the opposite direction.

basic cations but that through plant growth much hydrogen is active in weathering the mineral reserves and passing their nutrients to the growing crops. Here are the conditions that invite the prairie grasses. These grasses survive under the moderate rainfalls and find in the soil the essential fertility coming from mineral breakdown that constructs the vegetation of compounds more nourishing as feed than is the wood or even leaves of forest trees.

But when higher rainfall and temperature develop the soil until it is largely clay, with a few coarse mineral particles that are mainly quartz, these mineral fragments are of no significant value as nutrient reserves to be weathered by the acid clay. Consequently, the natural crop on such highly developed soils is forests. Forest trees nourish themselves by gathering fertility at a slow rate from rock breakdown as their roots penetrate more deeply. But they probably nourish themselves much more by rotating their fertility from the annual drop-

ping of leaves to the soil, whence they return it again into tree growth.   Highly
developed soils hold little fertility on their hydrogen-saturated clay, and are
delivering at a very slow rate small amounts from the mineral nutrient reserves
held in the small portion of the silt fraction that is other than quartz.

This ecological pattern suggests that the prairie soils are fertile and productive,
because their sands and silts are unweathered rock fragments other than quartz.
These sands and silts represent reserves of fertility to be weathered or broken
down for nutrient release.   Such soils are productive because on their significant
amounts of a moderately acid clay are stored fertility reserves in available and ex-
changeable forms, while more is being mobilized from the fertility reserves.   This
mobilization is the result of root action and microbial activity, with their result-
ing acidity or hydrogen going to the clay as the agency weathering the nutrient
mineral reserves.   It is in these mineral nutrient reserves, then, of the fragments
of other-than-clay minerals that the basic, potential fertility of our soils lies.

When the use of limestone on our soils is considered in terms of crop behavior
rather than in terms of the degree of soil acidity, the soil need not be considered
as a medium of infinite uniformity approaching molecular dimensions.   It need
not be considered as containing all the necessary plant nutrients within every
small unit of soil volume, when the application of a fertilizer in the bottom of
alternate plow furrows is about as effective as when application is made in every
furrow (8), nor when the work of Marshall suggests the highly buffered activity of
calcium adsorbed on the clay and its much greater activity in the calcium-
saturated, interfacial areas between a limestone particle and the surrounding
clay (6).   It would not seem a stretch of the imagination to believe that plant
roots might search out the more widely separated foci of different mineral frag-
ments around which the clay is saturated by their particular nutrient offerings.
One need not believe the plant unable to grow unless all the clay is uniformly of a
specific degree of acidity.   It seems more reasonable to believe that the plant is
growing much better if its advancing roots find one area around a limestone parti-
cle that may be nearly neutral but providing much calcium, then at some distance
another area more acid, where iron can be taken, then another acid area where
around some feldspar its potassium is slowly made available, then another where
the acidity is mobilizing the phosphorus, and still others where manganese and the
different essential nutrient elements are on the clay in exchangeable form because
the clay is in contact with some mineral fragment and maintains itself in a
weathering equilibrium with it.   If this is the proper concept of the soil-plant
relationships then it is easier to understand how the coarser or granular particles
of limestone can be more effective in growing sweet clover as green manure for
the corn crop than is 100-mesh limestone or even the sulfate and the very soluble
chloride of the calcium taken up readily and held in exchangeable form on the
clay.

SUMMARY

The use of 10-mesh limestone, 100-mesh or pulverized limestone, calcium sul-
fate, and calcium chloride as calcium fertilizers for establishing sweet clover

showed that the smaller applications of the 10-mesh limestone were relatively most effective as measured in corn yields. In heavier rates of application of limestone, at 2 tons per acre, the 10-mesh limestone was more effective than the 100-mesh materials alone, or than these in combination with phosphatic and potassic fertilizers.

These facts support the concept that the soil need not be a uniform medium as to degree of acidity or as to the distribution of all of the essential plant nutrients. Rather, the soil may be a mixture representing a heterogeneous collection of foci of each of these in the mineral or rock forms weathering slowly while in contact with the acid clay. Plant growth may then represent the summation of root contacts with all these different centers of fertility as the roots move to and get from them all that is needed for maximum crop productivity. According to this concept, both the very soluble and the less soluble nutrient materials applied in granular form would maintain this seemingly beneficial heterogeneity of fertility sources for better plant growth than would any practice aiming to blend the soil to the uniformity with which nutrient solutions are endowed. This concept points to possible trouble in saturating the clay with calcium only, which would displace other essential elements. It suggests also an economy in limestone use when this fertilizer stone will serve without the extra cost of its finer grinding.

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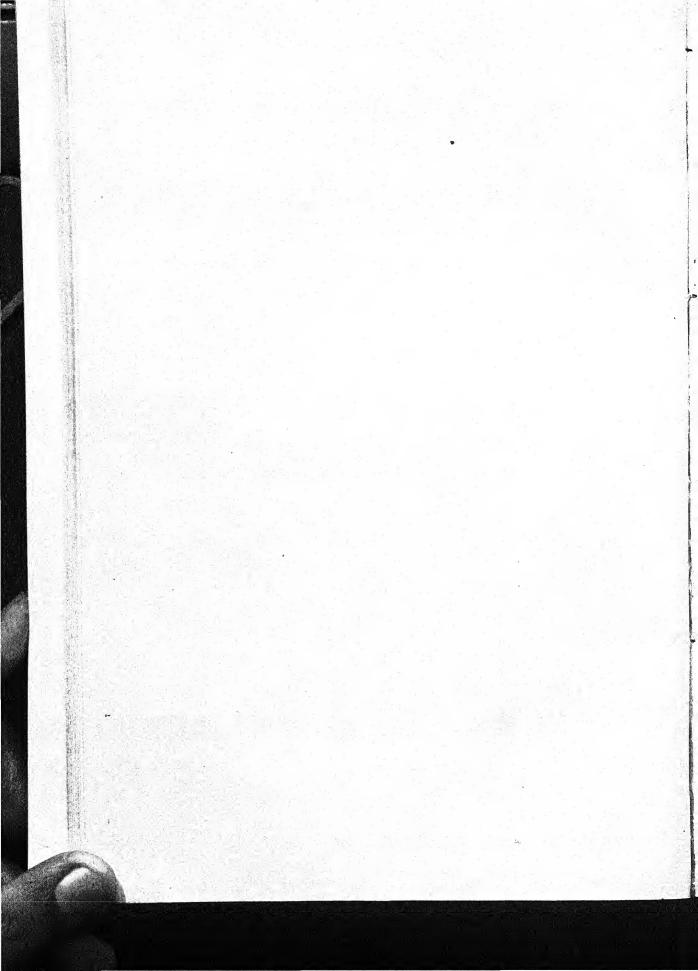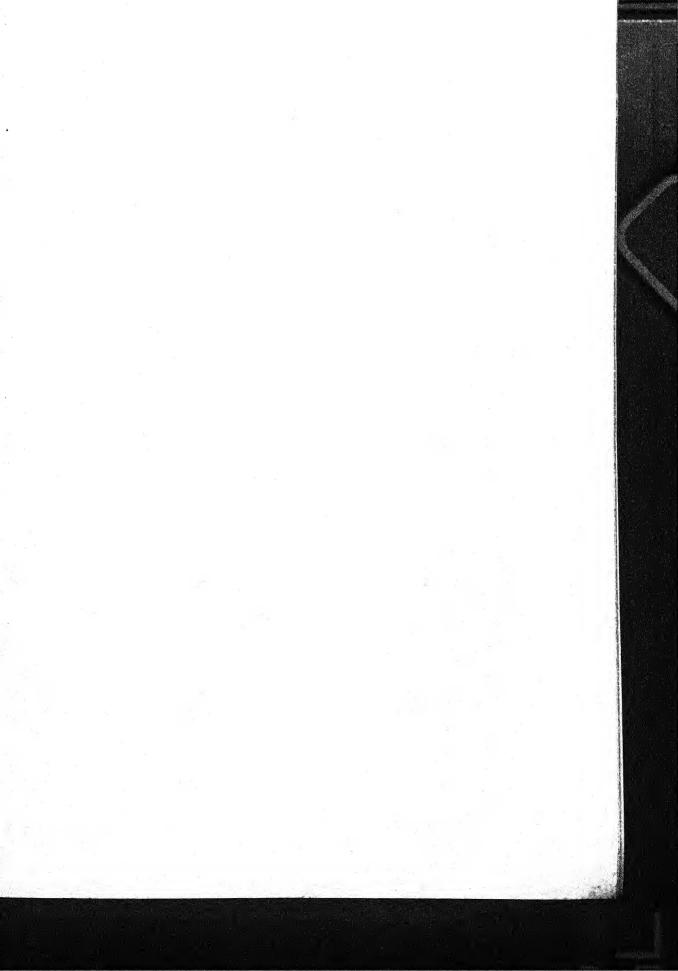
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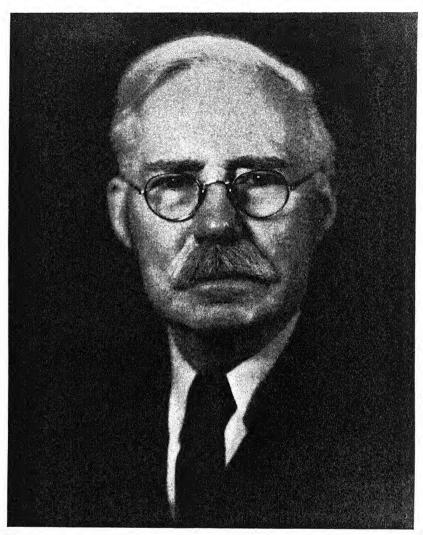
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Andrew Robeson Whitson
1870–1945

Andrew Robeson Whitson
1870 – 1945

Andrew Robeson Whitson, emeritus professor and for 38 years head of the soils work at the University of Wisconsin, died suddenly on November 20, 1945, at Madison, Wisconsin, where he had lived ever since joining the University faculty. Born on a farm near Stanton, Minnesota, October 9, 1870, he had reached the age of 75. His parents were pioneer Scotch settlers.

He took his college preparatory work at Carleton College, and then attended the University of Wisconsin for two years. During this time, under the influence of President T. C. Chamberlin, his interest in geology grew to such an extent that he transferred to the University of Chicago following Chamberlin's appointment as professor of geology at that institution. Here he received his bachelor's degree in 1894. During the summers of 1892 and 1893 he was field assistant with the U. S. Geological Survey and the Survey of the State of New Jersey, his work being a study of glacial and residual deposits and postglacial stream erosion. After a year of graduate work at Chicago, Whitson served as principal of the high school and instructor of sciences at Beloit, Wisconsin, from 1895–1899.

During the summers of 1897 and 1898 he carried on research in agricultural physics at Wisconsin with Professor F. H. King, and this led to an appointment in the fall of 1899 as assistant professor of agricultural physics at Wisconsin. In further preparation for this appointment, Whitson returned to the University of Chicago until the following spring for special studies related to soils and crop production. In 1901 Professor King joined the U. S. Bureau of Soils, and Whitson was made a full professor and head of the department.

Because of his broad training in physics, chemistry, botany, and geology and his early farm experience, Professor Whitson was quick to foresee that the application of lime and fertilizer to the soils of the state would in a short time be necessary for a successful and permanent agriculture, and that the teaching and study of soils should include not only soil physics but also soil chemistry, soil fertilization, and soil classification and mapping. Accordingly, at his request, general agricultural physics, which included agricultural engineering, was divorced from the department in 1905, and the name of the department was changed to the "Department of Soils" which was to include all phases of soils teaching and research. This was the first department in the country so organized, and Whitson became our first educator with the title of "Professor of Soils."

In 1907 he took a sabbatical leave and for the ensuing year studied sciences and agriculture in Germany and other European countries. While in Europe he was appointed by James Wilson, Secretary of Agriculture, to represent the United States as a delegate to the International Congress of Agriculture at Vienna.

Although demands for the teaching of elementary courses were always heavy, Professor Whitson, nevertheless, gave due attention to research and advanced study and encouraged and guided many students who later became prominent in their field of work. He was among the first in the country to make extensive

nitrate determinations of soils and to relate the results to the protein content of crops grown on these soils. Already in 1906 he was investigating soil acidity, liming, and availability of phosphates. The need of potash on peats and mucks had been investigated at an earlier date. Details of this early work are published in the annual reports of the Wisconsin Experiment Station.

For some 25 years, Whitson devoted much of his time and energy to the supervision of the State Soil Survey, which he was instrumental in getting formally started in 1909. During this time detailed soil maps and reports were made for more than half the counties of the state, and reconnaissance maps and reports for the remainder.

His interest and activity in soil survey work prompted him to recognize the need of greater unification of methods and aims the country over in this field, and this led to his leadership in the organization of the American Soil Survey Association. He was a charter member and fellow of the American Society of Agronomy and a member of the Wisconsin Academy of Sciences, Arts and Letters, of the American Association for the Advancement of Science, and of Sigma Xi.

Because of the interest in soil management which Whitson was instrumental in developing throughout the state, the legislature in 1912 made an appropriation for the creation of a soil-testing laboratory. Through this service, which has since been in continuous operation, some 6,000 farmers or farm owners in Wisconsin have been enabled to obtain detailed chemical and physical surveys of their land, and possibly close to half the farmers of the state have been reached.

Whitson was author and coauthor of several books and many bulletins, circulars, technical papers, and reports which have contributed much to the current knowledge of soils and their relationship to crop production. Since retirement he had been working on the manuscript for a book on soils and climatology, which at the time of his death, he had nearly completed. One of his early and continued interests dealt with the problems of soil erosion. A bulletin prepared 30 years ago by Whitson and Dunnewald, "Keep Our Hillsides from Washing," warned of the dangers of careless systems of cropping and explained cropping systems and other practices which would greatly lessen soil losses.

Withal his great interest in science and his broader interests in world affairs, Whitson was nevertheless a man of deep emotional motives. He loved and appreciated the finer things in life—music, literature, and art—and more than all else, he was sympathetic and understanding. In times of distress and trouble his friends and associates found him ready and willing to lend a helping hand. He took a great personal interest in the welfare of his students and colleagues.

EMIL TRUOG.

LOSSES OF NITROUS NITROGEN FROM SOILS ON DESICCATION

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Temple (3), Turtschin (4), and Fraps and Sterges (2) have reported the rapid decomposition of nitrites in acid soils. During studies on the losses of nitrogen in soils, it was noticed that if a soil with a pH value higher than 7 was allowed to dry, a part of the nitrous nitrogen disappeared. This could be attributed to one of the following causes:

1. Oxidation of nitrous nitrogen to nitric nitrogen.
2. Reduction of nitrous nitrogen to NH_3.
3. Assimilation of nitrous nitrogen by soil microorganisms.
4. Decomposition of nitrous nitrogen.

With a view to throwing light on the reactions that might be responsible for the observed disappearance of nitrous nitrogen from soils, the following experiments were conducted. The soils used in these experiments had a pH value of 8.7 unless otherwise stated.

EXPERIMENTAL

Effect of desiccation

Four 50-gm. portions of a sieved sandy loam soil were taken in enamelled iron dishes. Two portions were treated with enough $NaNO_2$ solution to supply 5 mgm. nitrogen per 100 gm. of soil. All four samples were brought to optimum moisture content (10 per cent) and exposed to the sun for a day. They were then analyzed[1] for mineral nitrogen. The results, given in table 1, show that a major portion of the added nitrite disappeared from the treated soil on desiccation and this loss was neither due to the oxidation of the nitrite to nitrate nor to its reduction to NH_3.

The experiment was repeated with clay loam soil and with a 10-mgm. treatment of nitrous nitrogen per 100 gm. of soil. In this case about 5 per cent of the nitrous nitrogen was oxidized.

In order to determine whether the disappearance of nitrous nitrogen was due to its assimilation by microorganisms, the experiment with clay loam soil was repeated at 90°C., a temperature at which little bacterial action could take place. The results, given in table 2, show that nitrous nitrogen is actually lost from the soil, not being retained in any other form, and that the reaction is not biological.

Since nitrous nitrogen is actually lost from the soil on desiccation, evidently it undergoes decomposition into gaseous nitrogen or its oxides or both. Ammoniacal nitrogen was present only in traces in the soil (table 1), and therefore the ob-

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[1] Nitrous nitrogen was determined by Griess Ilosways' method; nitric nitrogen by the phenoldisulfonic acid method; and ammoniacal nitrogen by distillation with freshly calcined magnesia (1).

served loss of nitrous nitrogen could not be attributed to the interaction of nitrous nitrogen with ammoniacal nitrogen, although this possibility cannot be excluded altogether.

The other alternative, that is, the decomposition of nitrous nitrogen with the evolution of nitrous fumes was next examined. A desiccating soil containing 10 mgm. nitrous nitrogen per 100 gm. soil was actually found to smell of nitrogen peroxide. A filter paper moistened with Griess Ilosways' reagent held over the soil quickly turned pink, while a control filter paper held at a distance in the air developed only a faint pink color during the same interval. This was further confirmed by desiccating the nitrite-treated soil by passing dry air through it and then bubbling the issuing air through soda solution. The soda solution in this

TABLE 1

Effect of desiccation on nitrous nitrogen of the soil

N in milligrams per 100 gm. soil

TREATMENT*	NH$_4$-N	NO$_2$-N	NO$_3$-N
Soil + 5 mgm. NO$_2$-N	0.75	1.02	1.6
	0.75	0.96	1.6
Soil only................................	0.84	0.01	1.6
	0.84	0.01	1.6

* After exposure to the sun for a day.

TABLE 2

Effect of desiccation at 90°C. on total nitrogen content of the soil

N in milligrams per 100 gm. soil

TREATMENT	NO$_2$-N	TOTAL N
Soil only........................	tr.	17.5
	tr.	18.2
	tr.	16.8
Soil + 10 mgm. NO$_2$-N	1.6	18.9
	1.6	18.9
	1.6	18.9

case was found to contain about 2 mgm. of nitrous nitrogen, while an equal volume of air aspirated through the blank contained only 0.01 mgm. nitrous nitrogen. There is some possibility of elemental nitrogen also being given out along with the oxides of nitrogen, but this was not tested.

To determine how closely the phenomenon of nitrous nitrogen loss was related to the desiccation of soil, another experiment was conducted as follows: Two 50-gm. portions of soil containing 5 mgm. nitrous nitrogen and 5 cc. water each were placed in glass-stoppered bottles. Two similar samples of soil were placed in glass dishes. All four samples were kept in the oven at 84°C. for about 14 hours and then analyzed for nitrous nitrogen. The results (table 3) show that about 9 mgm. of nitrous nitrogen was lost from each soil sample dried in an open

dish but that there was only a slight loss of nitrogen (less than 1 mgm. each) from the soils in the stoppered bottles. These results demonstrate that the loss takes place only during desiccation.

To study the effect of the concentration of nitrous nitrogen in soil on losses during desiccation, soil samples containing different amounts of nitrous nitrogen (2, 5, and 10 mgm. nitrogen per 100 gm. soil) were dried at 80°C. and analyzed for nitrous nitrogen. The loss of nitrogen was found to be proportional to the concentration of nitrous nitrogen (table 4).

TABLE 3

Losses of nitrous nitrogen from soils kept at 84°C. in stoppered bottles and in open dishes

N in milligrams per 100 gm. soil

TREATMENT	NO_2-N IN SOIL	LOSS OF NO_2-N
Soil + 10 mgm. NO_2-N kept in stoppered bottles..................................	9.1	0.9
	9.1	0.9
Soil + 10 mgm. NO_2-N kept in open dishes	0.9	9.1
	0.8	9.2

TABLE 4

Effect of concentration of nitrous nitrogen on its losses from soil

N in milligrams per 100 gm. soil

NO_2-N ADDED	NO_2-N IN SOIL	LOSS OF NO_2-N
2	0.19	1.81
2	0.17	1.83
5	0.26	4.74
5	0.24	4.76
10	0.48	9.52
10	0.48	9.52

Effect of nature of soil

To determine the effect of the nature of the soil on the loss of nitrous nitrogen, an experiment was conducted in the usual way with four different soils of varying pH. Each soil was treated with nitrous nitrogen to supply 10 mgm. nitrogen per 100 gm. soil and dried at 80°C. The results showed that the losses of nitrous nitrogen vary in different soils and take place even at a pH of 10.1 (table 5).

A sample of clay loam soil used in the previous experiment was converted into a barium soil by leaching with $Ba(OH)_2$ solution. Another sample of the same soil was treated with calcium oxide at the rate of 0.5 per cent, rubbed well into a thin paste with water, and dried in a thin layer. Still another portion of the same soil was ignited at 550°C. for about 6 hours. A fourth portion was left untreated. In all four soil samples the losses of nitrous nitrogen on desiccation were determined as before. The results, given in table 6, show, first, that losses of nitrous

nitrogen took place in all soils and that they were comparatively smaller in the prepared soils than in the original sample; second, losses took place in the ignited sample, showing that besides soil colloids some other factor was also responsible (losses observed to take place in purified sand confirmed this assumption); third, losses of nitrous nitrogen can take place in completely saturated soils.

TABLE 5

Losses of nitrous nitrogen from different soils on desiccation

N in milligrams per 100 gm. soil

SOIL	pH	NO_2-N IN SOIL	LOSS OF NO_2-N
Sandy loam + 10 mgm. NO_2-N..............	8.7	2.4	7.6
	8.7	2.6	7.4
Clay loam + 10 mgm. NO_2-N...............	8.7	1.1	8.9
	8.7	1.2	8.8
Saline soil* + 10 mgm. NO_2-N..............	9.5	1.9	8.1
	9.5	1.9	8.1
Alkali soil† + 10 mgm. NO_2-N..............	10.1	7.7	2.3
	10.1	7.7	2.3

* Contains 1.2 per cent water-soluble salts (mostly sodium chloride, sulfate, and carbonate).

† Exchange complex nearly saturated with sodium.

TABLE 6

Losses of nitrous nitrogen from differently treated soils on desiccation

N in milligrams per 100 gm. soil

SOIL	pH	NO_2-N IN SOIL	LOSS OF NO_2-N
Untreated soil.............................	8.7	1.2	8.8
	8.7	1.1	8.9
Barium soil + 10 mgm. NO_2-N..............	9.7	6.7	3.3
	9.7	6.7	3.3
Limed soil + 10 mgm. NO_2-N..............	10.1	5.3	4.7
	10.1	5.3	4.7
Ignited soil + 10 mgm. NO_2-N..............	10.7	3.0	7.0
	10.7	3.4	6.6

Chemistry of the reaction

The fact having been established that nitrous nitrogen is lost from soils on desiccation, a number of experiments were conducted to study the chemistry of the reaction.

The decomposition of the nitrite in soil during desiccation may be brought about by any one of the following factors:

1. Carbonic acid of the air.
2. Ammonia present in the air.
3. Exchangeable hydrogen of the soil.
4. Catalytic action of some soil constituents.

Effect of CO₂ on losses of nitrous nitrogen. Two 100-gm. samples of soil and two of purified sand, each containing 10 per cent moisture and 10 mgm. nitrous nitrogen, were dried at 80°C., one sample of each by means of air passed through a tower containing soda flakes, and the other by air passed through a tower containing $CaCl_2$. Exactly the same amount of air was aspirated in each case. The results (table 7) show that CO_2 of the air is responsible for a part of the loss.

Effect of NH₃ on losses of nitrous nitrogen. The technique of the experiment was the same as that of the previous study. Air for both samples of each soil was passed through a tower containing soda flakes, but in one case it was first passed through a tower containing pumice stone moistened with H_2SO_4. It was found (table 8) that the losses were slightly greater in the presence of atmospheric NH_3 than in its absence. The losses of nitrous nitrogen in the presence of NH_3 in this case were apparently brought about by the formation of NH_4NO_2, which decom-

TABLE 7

Effect of CO₂ on losses of nitrous nitrogen from soils on desiccation

N in milligrams per 100 gm. substrate

SUBSTRATE	NO_2-N IN PRESENCE OF CO_2	NO_2-N IN ABSENCE OF CO_2	LOSS OF NO_2-N DUE TO CO_2
Purified sand + 10 mgm. NO_2-N............	7.2	8.2	1.0
Clay loam soil + 10 mgm. NO_2-N..........	1.0	2.4	1.4

TABLE 8

Effect of NH₃ on losses of nitrous nitrogen from soils on desiccation

N in milligrams per 100 gm. soil

NO_2-N IN SOIL BEFORE DESICCATION	NO_2-N IN PRESENCE OF NH_3	NO_2-N IN ABSENCE OF NH_3	LOSS OF NO_2-N DUE TO AMMONIA
10	2.8	3.6	0.8
10	3.4	3.8	0.4

posed, with the evolution of gaseous nitrogen, at the high temperature prevailing in the experiment.

Effect of exchangeable hydrogen of soil complex on losses of nitrous nitrogen. It is a well-known fact that exchangeable hydrogen may be present even in soils with a pH value higher than 7.0. In that case it is possible that the exchangeable hydrogen liberates nitrous acid, which is subsequently decomposed on desiccation, resulting in a loss of nitrogen.

Losses of nitrous nitrogen through the action of soil catalysts. Two 50-gm. portions of a clay loam soil were each moistened with 5 cc. of $NaNO_2$ solution containing 5 mgm. of nitrous nitrogen and put in test tubes about 1.5 inches in diameter. One tube was tightly corked with a rubber stopper, and the other was left open. Both tubes were put in a filtration flask containing concentrated H_2SO_4. The flask was corked and placed in a water bath kept at 80°C. and then attached to a filter pump. Desiccation was carried out for about 16 hours.

A similar experiment was conducted with purified sand (digested in HCl and ignited). In this case, however, after 8 hours' desiccation, the open tube containing sand was remoistened with distilled water free from CO_2 and NH_3, and the desiccation was continued.

The contents of the tubes were analyzed for nitrous nitrogen. The results (table 9) show that desiccation of soil and sand in the absence of air also brought about losses of nitrous nitrogen. It would seem that the decomposition of nitrous nitrogen in purified sand in the absence of air is a case of catalytic decomposition. Thermal decomposition of $NaNO_2$ in the absence of catalysts was found to be inappreciable at temperatures below 100°C. Since the losses are greater in soil than in sand, it is likely that other constituents of the soil also act catalytically.

In the foregoing experiments, the losses of nitrous nitrogen from a clay loam soil on desiccation were roughly about 8 mgm. out of 10 mgm., whereas the losses due to CO_2 and NH_3 were only about 2 mgm. Thus it appears that catalytic decomposition of nitrous nitrogen in soils is nore important than decomposition by any other factors.

TABLE 9

Losses of nitrous nitrogen from soil on desiccation in a vacuum

N in milligrams per 100 gm. soil

SOIL	OPEN TUBE		STOPPERED TUBE	
	NO₂-N in soil	Loss of NO₂-N	NO₂-N in soil	Loss of NO₂-N
Clay loam soil + 10 mgm. NO₂-N.............	2.6	7.4	8.6	1.4
	2.4	7.6	8.9	1.1
Purified sand + 10 mgm. NO₂-N.............	5.3	4.7	9.6	0.4

SUMMARY

It has been shown that, on desiccation, nitrous nitrogen is lost from soils having pH values higher than 7. The phenomenon is purely chemical. The degree of loss varies directly as the concentration of nitrous nitrogen. The losses vary in different soils and may take place in soils with as high a pH value as 10.7.

Among the factors found to be responsible for the losses were CO_2 and NH_3 of the air, exchangeable hydrogen of the soil, and catalytic action of some soil constituents. Purified sand was found to act catalytically.

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A CRITIQUE OF ESTIMATING SOIL SOLUTION CONCENTRATION FROM THE ELECTRICAL CONDUCTIVITY OF SATURATED SOILS[1]

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For a half century, electrical conductivity measurements on saturated soil pastes have been used to estimate the soluble salt content of soils. In 1897 Whitney and Means (11) published a description of a portable Wheatstone bridge and procedures for this determination. Davis and Bryan (2, 3) improved the bridge for soils investigations and developed a table relating electrical resistance readings to salt content. A cylindrical soil conductivity cell of 50-ml. capacity, made of hard rubber, with two massive electrodes of nickel-plated brass extending the full height of the cell, has become known as the "Bureau of Soils cup." The determination of soluble salts by this technique has been employed extensively in soil surveys because of its rapidity and adaptability to field use. Several other portable bridges have been developed more recently. A soil cup having small platinized platinum disk electrodes was described by Scofield (9). Subsequently, a dip cell made of lucite plastic with parallel platinized platinum bands was described by Wilcox (13).

As the understanding of alkali soils progressed, attention became focused more on the concentration of the soil solution as directly affecting plant growth than on the total salt content on a weight basis. Scofield (9) concluded that it was preferable to report conductivity values than salt contents estimated from tables, because of variable salt composition and variable toxicity of different salts. The writers concur with this opinion.

The development of the concept that the stress of excess soluble salts is similar to that of a moisture stress has led to the use of osmotic pressure as an index of salt stress. Conductivity values of solutions usually are satisfactorily correlated with osmotic pressure values and thus provide a more rapid method of estimating the latter (1).

Measurement of the conductivity of a saturated soil paste had not been proposed as an accurate, but only as an approximate, index of salinity level. In recent years, accumulating evidence has led to a questioning of the accuracy attainable in the application of this method to estimation of soil solution concen-

tration.   These doubts have resulted in the investigations reported in this paper.
The direct application of the bulk of these results to the present procedure used
in soil surveys is not intended, as improvements in that technique would require
a somewhat different type of investigation.

EXPERIMENTAL METHODS AND RESULTS

Throughout this investigation, the relationship between the conductivity of a
soil paste and that of the solution phase within it has been regarded as a simple
fundamental expression of the reliability of the paste conductivity.   The con-
ductivity of the extracted solution is expressed by the symbol $Ke \times 10^5$ at 25°C.,
and that of the soil paste by $Ks \times 10^5$ at 25°C.   [K = specific electrical conduct-
ance in reciprocal ohms per centimeter; 10^5 is a factor to eliminate awkward deci-
mals; 25°C. is the standard reference temperature.   Temperature corrections for
deviations from 25°C. have been made by application of a technique described by
Wilcox (13) and also by use of a temperature coefficient of 2 per cent per degree
Centigrade rise in temperature.]   The ratio Ke/Ks used in this report is the
quotient of these two quantities.   If this ratio were a constant for all soil condi-
tions, no problem would exist, as the conductivity of the soil solution at satura-
tion could be calculated from the paste conductivity by multiplying by this
constant ratio.   This paper is concerned with the magnitude and origin of devia-
tions of this ratio from constancy.   This ratio should not be confused with
resistance ratios which have been employed by Means (8) and by Davis and
Bryan (2, 3).   Although referring to conductivity measurements, these other
ratios are based on principles with which this investigation is not directly con-
cerned.

The soil solutions were extracted from the moist soils by filtration under
vacuum on a Büchner funnel or under pressure in a special filter press (7, 13).
Alternating-current bridges used included (a) a 1000-cycle Wheatstone bridge
assembly involving a slide-wire, resistance box, and ear phones (12); (b) a box-
type Wheatstone bridge of fixed resistance ratios with a 60-cycle a.c. galvanome-
ter (13); and (c) portable and 110-volt line electronic bridges with cathode-ray
tube visual null-point indicators.   Soil conductivity cells included a Bureau of
Soils cup, a Scofield cup, a 50-ml. cubic cell of which two ends were formed of
square brass electrodes, and a plastic soil dip cell with platinized platinum band
electrodes.   Cells for measuring the conductivity of solutions included the Bu-
reau of Soils cup, platinized pipette cells of 5-ml. capacity, and a plastic platinized
dip cell (13).   The criteria of saturation used were those listed by Scofield (9),
namely, distilled water was added to the soil with stirring until the soil flowed
slightly when the container was tipped, the surface glistened as it reflected light,
and the air was displaced.   A further criterion of this point is that the moist soil
barely drops off a spatula.   The saturation percentage is the moisture content of
the saturated soil based on soil oven-dried at 105–110°C.

Variation of cup "constant"

For accurate calculation of conductivities, a cell must possess a "constant,"
which is usually determined by measuring the resistance of a standard solution

of known conductivity. This resistance multiplied by the conductivity of the standard solution equals the cell constant. Subsequently, the conductivity of an unknown is determined by dividing its resistance into this constant. During this investigation, it was found that the Bureau of Soils cup, the cubic cell, and the Scofield cup when inadequately platinized do not have cell constants, but that their "apparent cell constants" increase with increasing concentration and conductivity. In table 1 are shown typical increases obtained for these three cups with a series of standard KCl solutions. Values for the same Scofield cup after replatinization are included for comparison. In the normality range 0.002–0.2, the platinized cup constant increased only 1 per cent, whereas the other three cup constants increased 12, 14, and 13 per cent, respectively. With other salts, the constant changes to a greater or less extent. This inconstancy results from polarization effects of the passage of the electric current, even though this is of 1000-cycle frequency. The platinization reduces the polarization and consequently the deviation in "cell constant." This subject will not be discussed in detail here; Jones and Bollinger (5, 6) have considered the design of cells and the effect of platinization at length elsewhere. Some measurements of unknowns

TABLE 1

Variation of cell "constant" with KCl concentration

KCl NORMALITY	BUREAU OF SOILS CUP	CUBIC CUP	SCOFIELD CUP UNPLATINIZED	SCOFIELD CUP PLATINIZED
0.002	0.247	0.246	1.096	1.069
0.005	0.248	0.250	1.099	1.070
0.01	0.251	0.252	1.112	1.073
0.05	0.258	0.258	1.162	1.075
0.1	0.264	0.277	1.194	1.078
0.2	0.277	0.280	1.233	1.079
0.5	0.287			1.091

and cell constants were made with added capacitance in parallel with the cell in order to improve the null-point observation, but these have not been included. The effect of temperature variation, within the range 10–32°C. on the cell constants of the Bureau of Soils cup and a platinized Scofield cup was found to be negligible.

This lack of a cell constant for the Bureau of Soils cup and for platinized cups that have suffered loss of platinization through abrading action of soil particles precludes the precise calculation of conductivities. The percentage rate of change is comparatively small, however, at the lower concentrations. Conductivity values reported herein which have been obtained from use of these cups have been calculated from cell constants approximated by interpolation on standard conductivity curves prepared from salts or mixtures of salts corresponding to those adjudged present in the unknowns.

Effect of saturation percentage on Ke/Ks ratio

In 1939–40, the Division of Irrigation Agriculture of the Bureau of Plant Industry made the soil salinity study of the Pecos River Joint Investigation.

Included in this study were determinations of saturation percentage, conductivity of the saturated soil (Ks), and conductivity of the saturation percentage extract (Ke) on hundreds of soil samples from lands adjacent to the Pecos River in New Mexico and Texas. Within the nine areas of the region, the soil samples were tabulated in the order of decreasing crop productivity. After the Ke and Ks values were entered in the table, it was found that Ke showed an extremely high inverse correlation with yield. The Ks values were much less satisfactorily correlated with yields.

From these results, Scofield (10) concluded that when the Ke value

. . .ranged below 400, there was little or no evidence of salt injury to any crop plant. In situations where the conductance of the extracts ranged from 400 to 800, the less salt-tolerant crop plants did not thrive and the choice of crops was limited to those of the more salt-tolerant group, such as cotton, sugar beets, alfalfa and some of the grains, and to cereals including the sorghums. These salt-tolerant crops may be grown, but seldom thrive or yield well, in situations where the extract conductances range from 800 to 1500. Where the conductances range above 1500 plant growth is limited to a few species of salt-tolerant grasses, succulents, shrubs, and trees.

For these samples, the Ke/Ks ratio varied from 1.08 to 4.74. The mean for each of the nine areas ranged from 1.94 to 2.98. This extreme range of values is the source of the poorer correlation with yield obtained for Ks values. If a soil sample from this region had a Ks value of 350, the minimum ratio of 1.08 would provide a Ke value of 378, while the maximum ratio of 4.74 would indicate a Ke value of 1660. In this extreme example, the predictable crop conditions would encompass all four of the classes established by Scofield.

Figure 1 indicates the relationship between saturation percentage (S per cent) and Ke/Ks ratio for 223 soil samples taken in the Barstow, Texas, area. The negative correlation is highly significant. Although the indicated relationship is curvilinear, the extra trouble involved in deriving the curvilinear regression is not justified. This hyperbolic relationship is typical of samples from all nine areas. With increasing saturation percentage, the solution phase increases in percentage by volume of the total volume of saturated soil, and consequently the conductivity of the soil paste tends to approach that of the extract. Although a chart of this nature reduces the possible range of Ke/Ks values to some extent, residual errors of considerable magnitude remain, especially at lower saturation percentage values. Because the irrigation water and soil solutions in the Pecos region are saturated with gypsum, the direct application of these results to non-gypsiferous soils is not advocated.

A similar study of the variation of the conductivity ratio with saturation percentage was made on 36 samples from the Salinity Laboratory's collection of western soils. This relationship is shown in figure 2. A significant negative correlation exists. The wide diversity of characteristics among these samples evidently reduces the significance below that obtained for the soils within a comparatively small area. The Ke/Ks ratio ranges from 0.5 to 4.8, a variation of almost tenfold. The mean ratio of 2.27 is 27 per cent lower than that of 3.13 for the Barstow samples, a difference which is attributed to the generally higher level
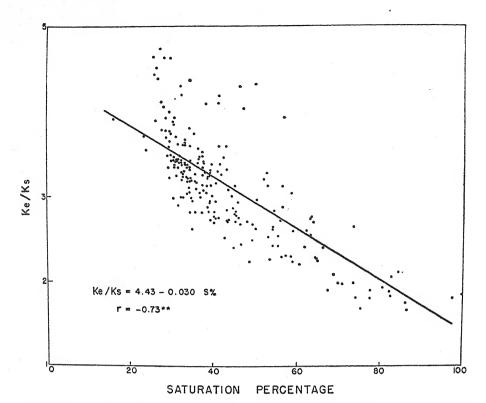
FIG. 1. EFFECT OF SATURATION PERCENTAGE ON THE Ke/Ks RATIO OF SOILS OF THE BARSTOW, TEXAS, AREA
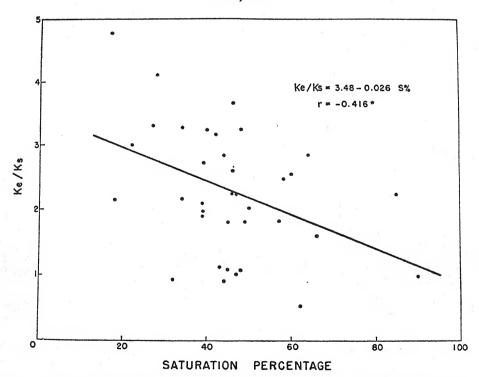
FIG. 2. EFFECT OF SATURATION PERCENTAGE ON THE Ke/Ks RATIO OF 36 WESTERN SOILS

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of salinity in the latter, as will be discussed in the next section.   The principle that saturation percentage affects the soil conductivity is involved in the division of soils into four texture groups; namely, sand, loam, clay loam, and clay, in the preparation of tables for soluble salt determinations (2, 3).

A better understanding of the effect of saturation percentage has been sought by means of washed quartz sand.   Pore-space percentage values between 31 and 54 were obtained in the Bureau of Soils cup through the use of variously graded screened separates and a range of compaction, and between 60 and 90 per cent by
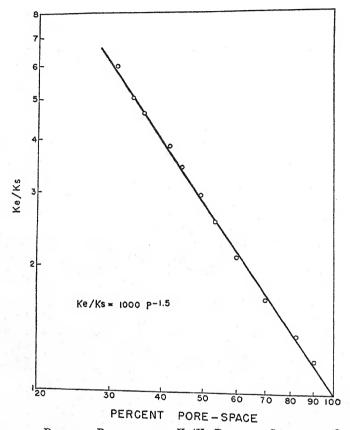
FIG. 3. RELATION BETWEEN POROSITY AND Ke/Ks RATIO OF SATURATED QUARTZ SAND

only partial filling of the cup with sand.   In this series, the cup was filled to the top with a 0.05 N NaCl solution having a conductivity value of 556.   The relation between Ke/Ks value and pore-space percentage (P) is shown in figure 3 to a logarithmic scale.   The equation indicated for this straight-line relationship is a theoretical hyperbola, which fits the experimental points surprisingly satisfactorily in view of the experimental errors involved.   The effect of the sand particles is not that of a simple reduction of solution volume.   In such a case, the controlling equation would be: $Ke/Ks = 100 P^{-1}$, that is, an equilateral hyper-

bola. This latter relation does obtain when the soil cup is partly filled with solution of volume equal to the porosity in question. The more complicated electrical pathways in the porous sand system exert an effect equivalent to a reduction in volume of solution. This effect must also exist in soils, but would be much more difficult to measure because of their less rigid, colloidal nature. With respect to the next section, it is of interest to note here that the Ke/Ks value of sand systems does not vary with the concentration of the solution used. A similar study has been made with a series of cylinders of plastics of increasing
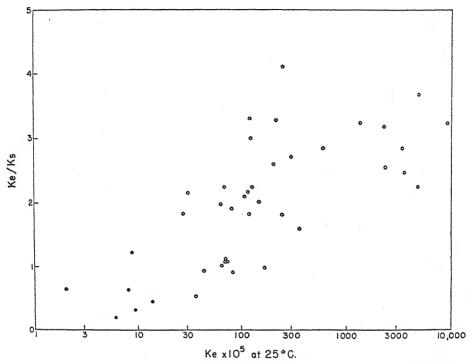
FIG. 4. EFFECT OF SOIL SOLUTION CONCENTRATION ON THE Ke/Ks RATIO OF 36 WESTERN SOILS

The solid black dots represent samples of six of these soils which were leached with distilled water to remove the naturally occurring salts.

diameter, but since the resistance varies with the position of the cylinder within the cup, the results are difficult to interpret.

Effect of soil solution concentration

The relationship between the Ke/Ks ratio of the 36 soils of figure 2 and their Ke values is shown to a semilogarithmic scale in figure 4. Although no correlation coefficient has been calculated, because of the tremendous range of Ke, it is apparent that the ratio increases with increasing Ke. The removal of salts by leaching has resulted in a minimum ratio of 0.2. It is also apparent, and even

more so on a rectilinear scale, that the rate of increase of the ratio decreases with increasing Ke value, that is, the ratio appears to approach a limiting maximum value at high concentrations. Concentration exerts a significant positive effect on the ratio even though the samples are of widely varying saturation percentage, the important effect of which has already been discussed.

To eliminate variation due to water-holding and other soil characteristics, similar studies were made on single soil types. In figure 5 are presented the results on a series of samples of Fallbrook loam (saturation percentage of 33) which
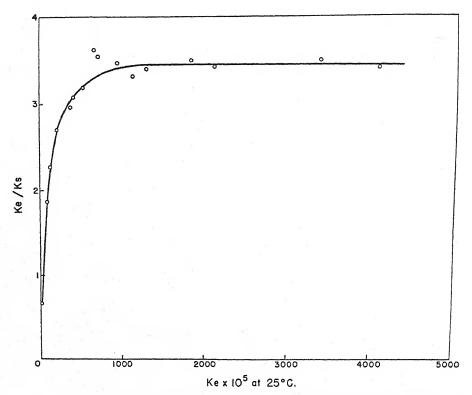
FIG. 5. EFFECT OF SOIL SOLUTION CONCENTRATION ON THE Ke/Ks RATIO OF FALLBROOK LOAM

had been used in a greenhouse experiment involving the response of beans to increasing concentrations of NaCl (1). Especially to be noted are the abrupt increase of the Ke/Ks ratio at low concentrations and an apparently limiting value of about 3.8. The scatter evident at Ke values between 700 and 4,000 is attributed to variation in cation composition occasioned by adding NaCl to a soil whose predominant exchangeable cation is calcium. The sample having a ratio of 0.65 is one of the leached soils of figure 4.

Two other soils, Fort Collins loam and Indio loam, were studied similarly by the addition of increasing amounts of a solution 0.2, 0.2, and 0.1 N in NaCl,

CaCl₂, and MgCl₂, respectively. The results for Fort Collins loam (saturation percentage of 42) are shown in figure 6. The relationship is the same as that for Fallbrook loam, but the scatter has been virtually eliminated by the use of salt of more uniform composition. A sample of Indio loam provided similar results.

The increase in Ke/Ks ratio with increasing salt concentration is regarded as a colloidal phenomenon. A large fraction of the conductivity of a soil colloid originates from the dissociation of the adsorbed ions, as electrically charged
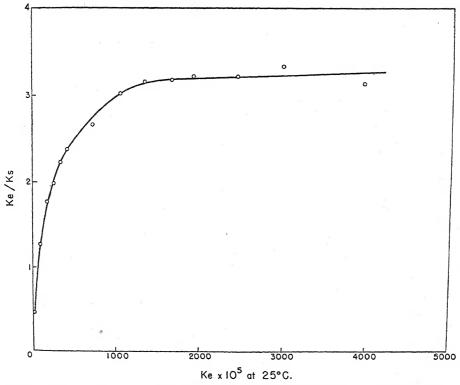
FIG. 6. EFFECT OF SOIL SOLUTION CONCENTRATION ON THE Ke/Ks RATIO OF FORT COLLINS LOAM

particles migrate during the passage of current. The addition of salt induces repression of dissociation of the adsorbed ions (4), a consequent decrease in conductivity, and an increase in the Ke/Ks ratio. Noncolloidal materials such as silica sand do not act in this manner but possess constant Ke/Ks ratios over wide ranges of concentration.

Effect of soil mineral conductivity

Because all substances conduct electricity to some extent, it was thought that some soil minerals might affect soil conductivity measurements by their own

inherent conductivity. Eleven minerals and salts immediately available at
the laboratory and that exist in soils or may act like soil minerals were washed
thoroughly with distilled water. They were then moistened to saturation (be-
cause of the different nature of these materials, this point does not accord with
the saturation percentage of soils and is not so reproducible), and after they had
stood several hours the Ks value was determined, the solution removed by vacum
filtration, and the Ke value determined. The results are presented in table 2.

Four materials possess Ke/Ks ratios of less than 1, which implies that the
conductivity of the material itself exceeds that of its saturated solution. Three
minerals, kaolin, magnetite, and iron pyrites, possess conductivity relationships
that indicate relatively high inherent conductivities. Of these three, only
kaolin or related minerals would be expected to occur in soils in appreciable
amounts, and the high conductivity may be a colloidal effect. It is concluded

TABLE 2

Conductivity relationships of minerals and slightly soluble salts

MATERIAL	SATURATION PERCENTAGE	$Ke \times 10^5$ AT 25°C.	$Ks \times 10^5$ AT 25°C.	Ke/Ks
Alumina (Al_2O_3)	26	1.80	1.86	0.97
Quartz sand	57	3.2	1.8	1.78
$BaSO_4$	58	5.04	2.73	1.85
$CaCO_3$	26	9.05	3.00	3.02
Magnetite ($FeO \cdot Fe_2O_3$)	15	12.5	29.7	0.42
Kaolin	92	14.9	16.0	0.93
Biotite	89	19.4	7.20	2.70
Fe_2O_3	96	31.6	21.8	1.45
$Ca_3(PO_4)_2$	216	45.0	30.4	1.48
Gypsum ($CaSO_4 \cdot 2H_2O$)	112	221	90.9	2.43
Iron pyrites	26	226	780	0.2?

that mineral conductivity is an important factor in soil conductivity measure-
ments only when the soluble salt content is extremely low.

Variation of soil conductivity with moisture content

All of the soil results discussed in preceding sections have been obtained on
samples moistened to the saturation percentage. The question is sometimes
raised, especially with regard to field measurements, as to the magnitude of
errors arising from undermoistening or overmoistening the soil. To obtain in-
formation on this point five soils were studied, of which two were gypsiferous.
The moisture content of each soil was varied considerably both below and above
the saturation percentage. The drier members of the series were subjected to
compaction by tamping in order to expel air and fill the pores with solution. The
Ke and Ks values of Cajon silty clay loam, typical of the nongypsiferous soils,
are shown in figure 7.

Over the entire moisture range, the Ks value is independent of the moisture
content. Throughout this range, however, the Ke value continuously decreases,
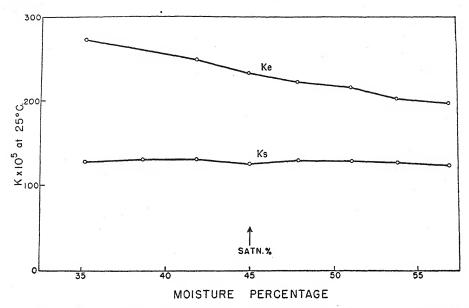
FIG. 7. EFFECT OF MOISTURE CONTENT OF CAJON SILTY CLAY LOAM ON SOIL AND EXTRACT
CONDUCTIVITY
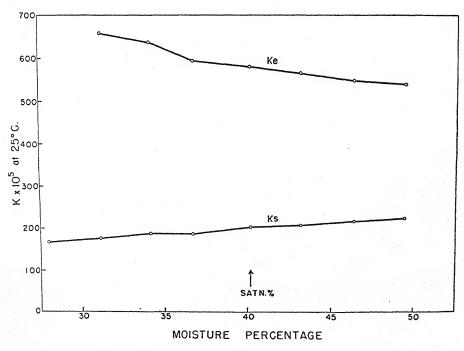
FIG. 8. EFFECT OF MOISTURE CONTENT OF REAGAN LOAM ON SOIL AND EXTRACT
CONDUCTIVITY

as could be predicted.   Evidently, on dilution, the decrease in solution concentration is closely counterbalanced by the percentage increase in volume occupied by the solution phase.   The Ke/Ks ratio changes in accordance with the change in Ke value.

In figure 8 are shown the same quantities for gypsiferous Reagan loam.   Because of the solubility of the excess gypsum, the Ks value of this soil increases substantially on extreme dilution.   For the same reason, the Ke value does not decrease to the same extent as in the Cajon soil.   It is concluded that in nongypsiferous soils considerable deviation in moisture content from "saturation" and in gypsiferous soils moisture deviations of several per cent will result in only slight errors in the soil conductivity determination.

CONCLUSIONS

The variability of the ratio between the conductivity of the saturation extract (Ke) and that of the saturated soil (Ks) is of such magnitude that the soil conductivity is unreliable as an index of soil solution concentration.   The extract conductivity is better correlated with crop response than is the soil conductivity. It has been shown that the Ke/Ks ratio increases with a decrease in saturation percentage and with an increase in extract concentration.   These two relationships appear to account for the greater part of the variation of this ratio.   Further investigation might clarify interreactions between these two effects and thus improve the reliability of the soil conductivity measurement.   The establishment of empirical calibration factors for the soils of a specific area might increase the precision of the method for use in that area.   It is concluded, however, that the extra effort involved in extracting the saturation soil solution is justified if a reasonable degree of accuracy is required.   These studies have not been directly concerned with errors arising from the extrapolation of saturation percentage results to lower moisture contents or from the variable composition of soluble salts.
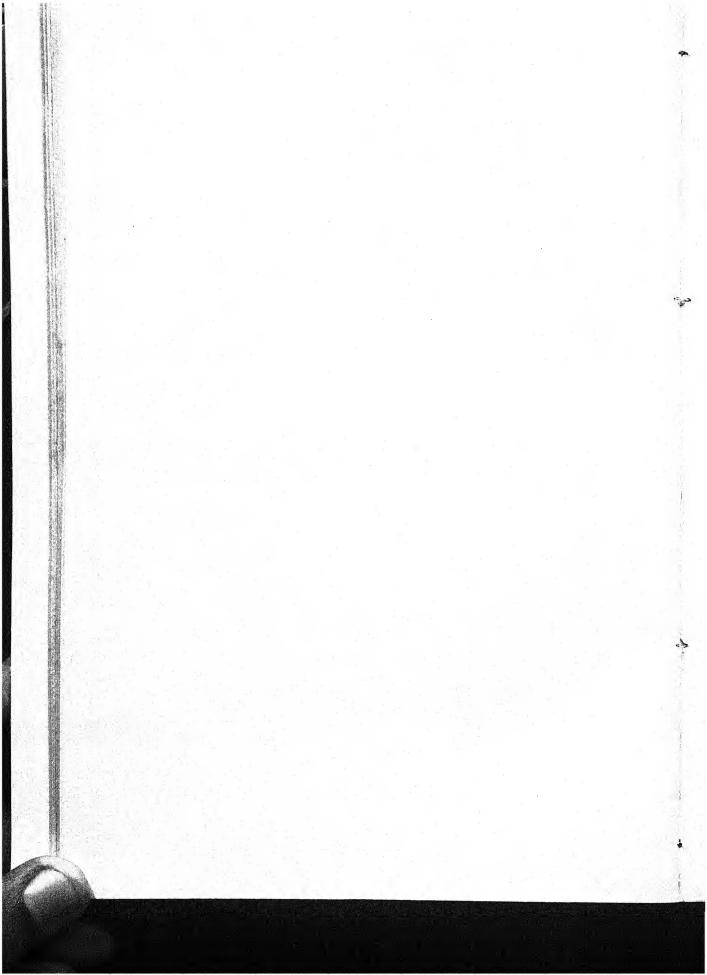
SUMMARY

The electrical conductivity of saturated soils is unreliable as an index of soil solution concentration.   Factors affecting the accuracy of this method include the lack of a cell constant for some soil cups, variations in saturation percentage, variations in soil salinity, and the conductivity of soil minerals.   When a reasonable degree of accuracy is desired, the solution should be extracted from the saturated soil and the conductivity of the solution measured.

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VARIANCE IN THE CARBONATATION OF CERTAIN "GLASSY" AND CRYSTALLINE CALCIUM SILICATE MATERIALS IN SOILS

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The extensive use of a relatively new type of quenched calcium silicate slag (8, 11) as a liming material has given rise to questions of both academic interest and practical importance. It had been established that the several types of calcium silicate undergo dissolution readily in carbonated water (2, 3, 9) and it was assumed that they would behave alike in soils. In pot cultures, however, the different silicate materials registered distinctively upon soil reaction and divergently in their effects upon plant growth (9). It was found that the mineral silicate, wollastonite, could be used without delimitation as to particle size and as to rate of incorporation, whereas the quenched calcium silicate slag from the phosphate-reduction furnaces could not. Incorporated under certain conditions as to fineness and rate, the quenched slag proved highly beneficial to plant growth, whereas under other conditions it proved virtually inhibitive. When comprised of material coarser than 60-mesh, the slag was used effectively at rates that proved disastrous when corresponding incorporations were finer than 100-mesh. The detrimental effects of the heavy incorporations of fine slag were transitory, however, and were succeeded by marked fertility (9). Moreover, when heavy-rate experimental quantities of 100-mesh slag were suspended in water and brought to equilibrium with CO_2 before incorporation with soil, the carbonatated fines became beneficial rather than repressive to plant growth. The present study of the conversion of calcium silicate materials to calcium carbonate and hydrated silica in soil systems was prompted by the foregoing observations and by the apparent relation between such conversion and the transition of a condition of virtual soil sterility to one of distinct fertility.

TYPES OF CALCIC SLAG

Since they come as by-products from distinct operations, slags vary in physical properties, in composition, in solubility by reagents, and in liming effectiveness. Some slags are air-cooled and then ground, and some are processed to fineness through quenching. In particular, calcium silicate slags should be differentiated from *basic slag*, or Thomas slag, primarily a phosphatic fertilizer. Moreover, nonphosphatic *blast furnace slag* should be distinguished from the *quenched calcium silicate slag* that comes from the electric rock phosphate-reduction furnace and contains 1.5 per cent of P_2O_5. Hence, when incorporated with soil at rates and of fineness consonant with those prescribed for limestone, the quenched calcium silicate slag supplies effective quantities of phosphorus (9, 10, 11).

The samples of rock-phosphate-furnace slag used in the present comparisons were obtained *solely* from the TVA operations at Wilson Dam.   When that slag is air-cooled in bulk, the resultant material is dense and visibly crystalline, in contrast to the "glassy" nature of the quenched product (8).   The perfection of the technique of jet-quenching obviated the otherwise expensive step of grinding and affords a proximately 20-mesh liming material, composed of brittle, pitted, thin-edged, "glassy" particles that undergo hydrolysis readily.

LIMITATION OF CHEMICAL ANALYSES IN EVALUATION OF SLAGS

The liming effectiveness of calcium silicate slags cannot be determined by means of the A.O.A.C. titrative procedure prescribed for caustic and carbonate liming materials (1), or on the basis of overall Ca content.   Slags are characterized by different percentages of sulfides, phosphates, Ca-Al silicates, and fluorides. All of these vitiate the analytical titrations, and the calcium that occurs in such combinations is not entitled to expression as $CaCO_3$-equivalence indicative of liming value.   It has been shown that proximate neutralization values can be established by potentiometric titrations and that reactive Ca content can be determined accurately by the recently adopted acetic acid procedure (14).

The analytically determined $CaCO_3$-potential of a slag does not afford an infallible index of its immediate liming effectiveness.   Alumina content, in particular, affects the rapidity with which a slag undergoes dissolution by reagents differing in strength and concentration.   On the basis of chemical analysis, two slags may appear virtually identical in potential neutralization value and yet not register alike in the soil system, as to elevation in pH and through plant response. Moreover, two slags may contain identical quantities of a particular silicate of calcium and yet be distinctive in reactivity, because of difference in structure. As noted, the slow cooling of a silicate slag induces crystallinity, whereas quenching imparts a "glassy" nature.   Although slags of like origin and physical properties can be arranged in groups by means of laboratory tests, individual slags of a group may possess inherent properties not indicated by their computed neutralization values, or by empirically determined capacity to neutralize acidic reagents.   Since it is conventional to use the term "$CaCO_3$-equivalence" in expressing the neutralization value of limestone or that of dolomite and in reporting the carbonate content of soils, that equivalence is intended in the present stipulations as to rates at which the several calcic materials were either incorporated or generated.

OBJECTIVE

The primary objective of this paper is to reveal the rapidity with which the calcium silicate components of certain quenched slags and similar "glassy" materials undergo disintegration, sorption, and conversion to $CaCO_3$ in soils, in contradistinction to the stability of crystalline isomers, although the two types of silicates possess the common property of ready solubility in carbonated water. Certain chemical aspects as to bicarbonate concentrations attained by carbonated water digestates of the carbonates and silicates of calcium, and also distinctive

effects of the several solids upon soil pH and upon crop response and plant composition, will be dealt with subsequently.

EXPERIMENTAL

The experimental essentials—range in the rates of incorporation and in particle size of the calcic materials, intervals between analyses of the treated soils, and fallow versus cropping—were introduced in the experimental setup of the present study. Appalachian marble was used as the limestone control. Quenched and unquenched portions of the same draw of phosphate furnace slag were used as respectively representative of the glassy and crystalline forms, in the comparisons with analogous experimental slags and with the raw crystalline mineral silicate, wollastonite, together with its calcines and its quenched and air-cooled melts.

TABLE 1

Neutralization values and partial analyses of the several liming materials

MATERIALS	CaCO₃ EQUIVALENCE	P₂O₅	FLUORINE
	per cent	*per cent*	*per cent*
Calcium silicate slags			
Quenched			
S-349 [1935].	87.5	1.40	3.10
S-693 [1939].	84.2	1.30	2.30
S-795 [1940].	84.1	1.30	3.20
S-1084 [1943].	82.1	1.30	1.88
Unquenched			
S-1083 [1943].	82.1	1.30	1.88
Experimental slags*, quenched			
Without CaF₂—S-920.	93.8	0.20	
With CaF₂ —S-921.	93.5	0.20	2.39
Limestone.	99.5	Tr	Tr
Wollastonite (CaSiO₃)† [S-1027].	82.0	Tr	Tr

* From fusion of a mixture of limestone and quartz and Al₂O₃ and Fe₂O₃, in simulation of by-product slag.

† The crystalline mineral contained 1.0 per cent of CaCO₃.

The liming materials were incorporated with soil at either half or full depth, in duplicated 2-gallon glazed pots in the greenhouse, and the cultures were watered periodically to the optimum. Partial analyses and proximate potential CaCO₃-equivalence of the several liming materials of table 1 and occurrences of carbonates were obtained by conventional A.O.A.C. methods (1), with the exception noted hereafter.

Effect of rate and fineness upon carbonatation of a quenched slag in cropped soil

The Montevallo silt loam of table 2 had received parallel full-depth incorporations of slag and limestone screenings at the 5-, 10-, 20-, and 40-ton rates and then was cropped nine times. An immediate objective had been to ascertain whether heavier incorporations of the initially somewhat coarse quenched slag would be

admissible and as effective as lighter incorporations of finer material, thus obviating the expense of grinding. Since the aspect of conversion of calcium silicate to $CaCO_3$ in the soil was not one of the several initial objectives of this experiment, the carbonate analyses of the five periodic samplings were not obtained until after the harvesting of the ninth crop. The heavy incorporations of the relatively coarse slag ($-20+60$ mesh) had proved beneficial to both immediate and subsequent plant growth, whereas the corresponding incorporations of 100-mesh screenings had proved virtually inhibitive to the initial seeding and were

TABLE 2

Accumulation of $CaCO_3$ from full-depth incorporations of a quenched calcium silicate slag in relation to residues of $CaCO_3$ from corresponding incorporations of limestone, in Montevallo silt loam

INCORPORATIONS			$CaCO_3$ PER 2,000,000 POUNDS OF SOIL PRESENT AFTER				
Material	Mesh	$CaCO_3$ per 2,000,000 pounds of soil	First crop— sweet clover	Sixth crop— sudan grass	Seventh crop—red clover	Eighth crop— sudan grass	Ninth crop— sudan grass
		lbs.	lbs.	lbs.	lbs.	lbs.	lbs.
Slag*	-100	10,000	500		700	600	900
Limestone†	-100	10,000	3,900	1,600	2,000	2,000	1,800
Slag	$-20+60$	20,000	1,600	2,500	3,200	5,000	3,600
Slag	-100	20,000	8,400	7,100	7,700	7,500	7,300
Slag	$-20+60$	40,000	4,300	7,500	8,000	8,200	6,600
Limestone	$-20+60$	40,000	35,000	33,400	28,400	32,500	30,900
Slag	-100	40,000	20,700	21,600	23,000	20,700	21,200
Limestone	-100	40,000	31,000	29,000	25,100	28,700	31,600
Slag	$-20+60$	80,000	9,600	12,300	11,100	13,900	12,300
Limestone	$-20+60$	80,000	70,500	71,000	55,100	67,100	61,900
Slag	-100	80,000	43,100	54,600	52,300	51,900	52,500
Limestone	-100	80,000	65,000	66,900	70,000	68,000	64,900

* All slag separates were screenings from S-349 of table 1.

† All limestone separates were screenings from an Appalachian marble of 99 per cent $CaCO_3$ content.

markedly repressive upon several successive crops. The initially injurious effect of the heavy incorporations of the 100-mesh slag was transitory, however, and was succeeded by marked fertility, the advent of which was inverse to the rate of incorporation (9, 10). It therefore appeared probable that the change from a condition of virtual sterility to one of fertility in the soil that had been slagged heavily with fine quenched material would be governed by the conversion of the silicate to the carbonate.

The periodic occurrences of carbonate, those cumulative from the 5-ton in-

corporations of 100-mesh slag and those residual from the companion incorpora-
tions of limestone, were fractional of the quantity of the $CaCO_3$ introduced by the
limestone.   The course and degree of the disintegration of the slag, therefore, was
not established by the periodic determinations of the CO_2 content of the soils of
the two series.   But the comparisons for the quantities of carbonate attributable
to the heavier incorporations of slag and limestone of like fineness did afford data
that indicated that most of the hydroxide of calcium derived from the 5-ton
addition of slag reacted directly with the soil acidoids and, therefore, the periodi-
cally collected samples of soil showed no significant occurrences of $CaCO_3$.   It
seems certain, however, that the soil system was enriched by sorption of the major
fraction of the Ca supplied by the 5-ton incorporation of 100-mesh slag, and that
this phenomenon occurred mainly during the growth of the initial crop, under
which 61 per cent of the 5-ton control incorporation of limestone suffered
decomposition.

The cumulation of $CaCO_3$ from the 10-ton incorporation of 100-mesh slag
exceeded by far the cumulation from the corresponding incorporation of the
$-20+60$-mesh separate at every period, the ratio being 5 to 1 after the initial
harvest.   The final occurrence of carbonate for the 20-ton incorporation of
$-20+60$-mesh slag was only about one-fifth of the amount residual from its
limestone control, whereas the final occurrence of $CaCO_3$ from the companion
incorporation of minus 100-mesh screenings of the slag was proximately two-
thirds of the residue of the 100-mesh limestone.

The ultimate incidence of $CaCO_3$ from the 40-ton incorporation of $-20+60$-
mesh slag was proximately twice that found for the 20-ton incorporation of that
separate, whereas the cumulation of $CaCO_3$ from the 40-ton incorporation of the
100-mesh screening was more than four times the cumulation from the companion
incorporation of $-20+60$-mesh slag.   Obviously, formation of $CaCO_3$ was
expedited when slag surface was increased through heavier additions and finer
material.   On the assumption that the soil sorbed virtually the same quantity
of Ca from the slag and the limestone, the ultimate incidence of $CaCO_3$ from the
40-ton incorporation of 100-mesh slag represented a degree of carbonation virtu-
ally the same as the ultimate induced when charges of pulverized quenched slag
were subjected to repetitive digestions in carbonated water, with intermittent
grinding of the transformed solids.   The resultant carbonate was 82 per cent of
the computed potential on the basis of total Ca content minus the fraction ac-
counted for jointly by F_2 and PO_4 combinations.

Variance in carbonatation of quenched slags and wollastonite

In several earlier laboratory studies (3, 8, 9) wollastonite was found to be
as readily soluble as was limestone in carbonated water, and the mineral silicate
proved even more effective than limestone in pot cultures of red clover (5).   The
pilot comparisons of table 3, therefore, were made to ascertain whether the min-
eral silicate and the quenched slag behave alike in their reaction with CO_2 in soil
systems.

A 15-ton cumulation of $CaCO_3$ came from a 35-ton incorporation of 100-mesh

quenched slag during the growth of a single crop of Sudan grass, whereas 4 tons of the control incorporation of 100-mesh limestone had suffered decomposition. In contradistinction, no enhancement in carbonate content occurred in the soils the had received the several parallel incorporations of either raw wollastonite or its calcines, x-ray patterns of which demonstrated that structure had not been altered by the calcinations. Hence, under the soil conditions, the inertness of the crystalline wollastonite toward moisture and CO_2 in the soil system was distinct from the ready dissolution of that mineral in carbonated water.

In general, rise in soil pH was induced by wöllastonite, limestone, and slag, in that order of ascension. The relative effects of heavy additions of raw and processed wollastonite upon soil pH, and absence of any repression exerted by the mineral upon plant growth, will be considered in a separate presentation.

The pilot comparisons were amplified as to the effect of particle size, and of rate of incorporation, upon the rapidity and extent of the carbonatation of three

TABLE 3

Variance in accumulation of $CaCO_3$ from incorporations of wollastonite, and of quenched slag, after a crop of Sudan grass on Hartsells soil

LIMING MATERIALS*	GAIN IN CaCO₃
	lbs.†
Wollastonite, raw, S-1027...................................	500‡
Wollastonite, 800°C. calcine................................	300
Wollastonite, 1100°C. calcine...............................	300
Slag, S-795...	31,100
Limestone..	69,700

* As 100-mesh screenings, at rate of 77,700 pounds $CaCO_3$-equivalence per 2,000,000 pounds of soil, mixed with upper half. Identical incorporations of K_2O, as K_2SO_4, and appropriate top-dressings of NH_4NO_3, were made.

† Per 2,000,000 pounds of soil.

‡ Not corrected for the 777-pound increment carried by the wollastonite.

samples of quenched slag and wollastonite, and upon the decomposition of the limestone controls in the upper half of two soils. The analyses were made after the harvesting of each of three successive crops, as given in table 4, and the slags were products of different years.

The small residues of carbonate from the 7,800-pound incorporation of 100-mesh limestone registered almost complete decomposition of that control, and there was no significant accumulation of carbonate from any of the 18 cases in which the three slags were incorporated with the two soils at that rate. On the other hand, a substantial cumulation came from every one of the 18 incorporations of slag at the three heavier rates, and there were substantial residues from the companionate incorporations of limestone. Again, therefore, it is indicated that at the 7,800-pound rate, most of the incorporated slag underwent hydrolysis and direct reaction with the soil and that any $CaCO_3$ formed on the surface of the slag particles was of short duration.

TABLE 4

Ready carbonatation of quenched calcium silicate slags and inertness of wollastonite in two soils under cropping

INCORPORATIONS*			CaCO₃† PRESENT AFTER SUCCESSIVE CROPS‡					
			Hartsells fine sandy loam			Baxter silt loam		
Material	CaCO₃-equivalence	Mesh	Sudan gass	Sudan grass	Red clover	Sudan grass	Sudan grass	Red clover
	lbs.†		lbs.	lbs.	lbs.	lbs.	lbs.	lbs.
Limestone		Unground§	4,300	3,600	2,300	5,900	4,500	3,600
	7,800	−20	3,400	2,500	2,300	3,900	3,000	2,300
		−100	1,100		200	2,000	1,400	900
	19,400	−100	12,300	13,400	10,700	12,700	13,000	10,200
	38,900	−100	30,000	30,700	28,200	32,300	37,100	26,400
	77,700	−100	64,400	64,000	61,000	68,200	70,100	63,900
Slag S-349		Unground		200	200	200		500
	7,800	−20						200
		−100						200
	19,400	−100	4,800	4,800	6,400	7,700	7,700	7,700
	38,900	−100	17,700	19,800	18,600	22,700	21,400	22,100
	77,700	−100	30,900	41,800	42,800	40,900	50,000	47,500
Slag S-693		Unground		200			700	
	7,800	−20			200	700		
		−100						
	19,400	−100	4,800	5,200	4,100	8,000	7,100	6,400
	38,900	−100	15,200	18,200	19,100	20,200	20,000	
	77,700	−100	25,000	37,100	42,300	29,600	45,700	45,900
Slag S-795		Unground		500	200		200	
	7,800	−20			500	200		200
		−100		200			200	200
	19,400	−100	4,100	4,300	4,100	6,100	6,800	6,400
	38,900	−100	12,100	16,100	14,600	20,200	21,400	20,000
	77,700	−100	25,500	33,200	32,500	37,100	38,000	43,400
Wollastonite‖		Unground§		700			900	
	·7,800	−20		200		900		
		−100				500		
	19,400	−100					500	200
	38,900	−100		200		200		700
	77,700	−100	200	200	500	900	900	500

* With the upper half of soil. All cultures received K₂SO₄ and the nonlegume cultures were top-dressed with NH₄NO₃ as needed.

† Per 2,000,000 pounds of soil.

‡ Analyses were made also after two more successive crops and gave results virtually the same as those obtained after the red clover had been harvested.

§ Mechanical make-up corresponded with that of each slag and was made identical to that of "unground" slag S-795, 98.7 per cent of which was finer than 10-mesh.

‖ Contained 1.0 per cent of CaCO₃, for which no correction was made in the analyses of the cultures that received wollastonite.

In general, the quantities of carbonate derived from the half-depth incorporations of the 100-mesh quenched slags at the rates of approximately 10 and 20 tons per acre-surface were much the same after initial and final croppings. Although the cumulations from the near-40-ton incorporations of 100-mesh slag did not reach the maximum during the growth of the initial crop of Sudan grass, every quantity of $CaCO_3$ then generated constituted a major fraction of the final quantity. Invariably, however, the ultimate cumulation of $CaCO_3$ was less than the amount residual from the corresponding limestone incorporation. The disparity might be attributed, in part, to pseudoequilibrium between the Ca-saturated soil systems and $CaCO_3$-silica-coated grains of slag, the coatings serving to protect unchanged nuclei. This attribution is not adequate, however, since, as noted, complete conversion of the silicate to carbonate did not obtain when pulverized slag was subjected to repetitive digestions in carbonated water, the transformed solids being ground during the intervals between digestions. Subjected to such treatment, calcium metasilicate is transformed completely to a mixture of $CaCO_3$ and hydrated SiO_2, whereas Ca-Al-silicate components in slags are resistant to hydrolysis and dissolution.

Again, as in the pilot comparisons of table 3, the heavy incorporations of raw wollastonite showed virtually no cumulation of $CaCO_3$, even after the growth of three crops and without correction for the 1 per cent carbonate content of the mineral silicate. Virtually identical results as to lack of carbonatation of the wollastonite were registered by supplemental analyses made after each harvest of two additional crops.

Effects of quenching and of fluoride content upon carbonatation of calcium silicate materials

In this experiment, the objectives were to ascertain the effects of quenching and of fluoride content upon the rapidity of the silicate-to-carbonate conversion. The unquenched slag (S-1083) and the quenched material (S-1084) were portions from the same draw of a 1943 slag (tables 1 and 5). A 1-ton portion was air-cooled 3 days and was crystalline, whereas the quenched portion was "glassy." These two slags were incorporated with two soils, in parallel with wollastonite—raw, air-cooled fusions, and quenched fusions—and with two experimental slags, obtained by the fusion of 500-pound mixtures of lime, quartz, F_2O_3, and Al_2O_3, in simulation of the furnace slag. One of the experimental slags was made to contain 4.9 per cent of calcium fluoride, whereas the other was made without inclusion of that compound. All silicate materials and the limestone were minus 100-mesh, with the exception of the "unground" quenched 1943 slag (S-1084), which was used as representative of the standard output.

Occurrences of $CaCO_3$ from the silicate materials and from the limestone were determined by the Shaw-MacIntire procedure (13) after each of the five successive harvests. It is apparent that the decomposition of the near-6-ton limestone control incorporations occurred chiefly during the growth of the initial crop, although the indication of subsequent decomposition may be significant. The residues from the 17.5-ton limestone incorporation were, however, reasonably uni-

TABLE 5

Variance in accumulation of $CaCO_3$ from incorporations of quenched and unquenched slags and wollastonite, subsequent to their incorporation with two successively cropped soils

Material‡	CaCO₃-equivalence	$CaCO_3$† present after each of five successive crops									
		Hartsells fine sandy loam					Fullerton silt loam				
	lbs.†	Sudan grass	Sudan grass	Red clover	Sudan grass	Alfalfa	Sudan grass	Sudan grass	Red clover	Sudan grass	Alfalfa
	lbs.	lbs.	lbs.	lbs.	lbs.	lbs.	lbs.	lbs.	lbs.	lbs.	lbs.
Limestone	11,700	3,300	3,300	2,600	2,000	1,500	4,600	3,000	3,400	2,800	2,500
	35,000	20,300	20,700	21,600	23,000	22,500	25,300	25,900	25,700	25,300	23,500
Slag, quenched, S-1084											
Unground	11,700	100	600	200	200		300	900	100	400	
	35,000	600	1,000	2,100	1,900	1,800	700	700	1,900	2,200	2,500
Ground	11,700	500	400	400	100	200			500	400	200
	35,000	10,800	11,200	12,400	12,900	13,500	8,200	9,600	10,100	10,500	12,000
Slag, unquenched, S-1083											
Ground	11,700	100	100	200	200	300	100	100	200	700	200
	35,000	2,600	2,700	2,800	3,700	5,000	1,800	2,900	7,800	8,400	9,200
Wollastonite, S-1027											
Raw	11,700	100	100	100				100	100	100	
	35,000	100	100	300	100	800		100	300	500	500
Fused and unquenched	11,700	200	100	100	100		8,600	100			
	35,000	7,200	8,300	9,300	9,600	10,100	13,900	10,800	12,700	12,000	11,500
Fused and quenched	11,700	200	300	100	100	300	700	500	200	100	
	35,000	10,000	11,000	12,400	10,900	12,300		12,700	12,900	13,100	12,200
Experimental slags§, quenched											
Without CaF₂, S-920	11,700	400	400	200		100	200	800	700	100	100
	35,000	6,400	6,100	6,300	6,300	7,500	9,200	7,700	8,000	6,900	8,000
With CaF₂, S-921	11,700	500	600	200	200	400	1,300	900		400	400
	35,000	13,000	12,800	13,300	12,000	13,000	14,100	14,000	14,300	13,600	14,000

* In upper half of soil.

† Per 2,000,000 pounds of soil.

‡ With the exception of the unground quenched slag S-1084, all materials were 100-mesh.

§ Of mixtures of Appalachian marble and quartz and Al₂O₃ and Fe₂O₃, in simulation of by-product slag.

form at the five periods. The small percentages of carbonate shown by the periodic analyses of the soils slagged with unground material at the near-6-ton rate probably reflect a sustained balance between soil and the $CaCO_3$-coated particles of quenched slag. In the companion comparisons with 100-mesh materials at this rate, however, the cumulations of $CaCO_3$ were not sufficient to establish distinction in the carbonate conversions. The decidedly greater reactivity imparted by the quenching is shown by the carbonate cumulations from incorporations at the 17.5 ton rate, those from the quenched slag S-1084 being greatly beyond those from the parallel incorporations of the air-cooled material. This disparity reflects the resistance of the air-cooled crystalline slag to hydrolytic disintegration in the soil, in contrast to the readiness with which the "glassy" quenched slag undergoes that disintegration.

Again, the carbonate content of the soil was not increased by the input of raw wollastonite and, in most cases, that content was even less than the amount attributable to the $CaCO_3$ impurity of the mineral. Thus, under the soil conditions of a low proportion of water to wollastonite and with relativly low partial pressure of CO_2, the mineral silicate proved resistant to hydrolysis and carbonatation, although, as noted, it undergoes dissolution rapidly when suspended in carbonated water (2, 3, 8, 9).

In contrast to the inertness of the mineral silicate, both of the laboratory melts of wollastonite registered substantial development of carbonate from the heavy-rate incorporations. Obviously, the melts had acquired structural characteristics distinctive from those of the raw material. Although the air-cooled portion of the laboratory melt of the relatively pure wollastonite (S-1027) proved less reactive than the quenched portion, it was far more reactive than the unquenched furnace slag, S-1083. The disparity between the reactivity of the air-cooled melt of wollastonite and that of the unquenched slag (S-1083) is too great to be accounted for by the deterrent effect of the component impurities of the slag, and probably is attributable to difference in content of crystalline silicates. Both of the materials were air-cooled, but in different bulks and, hence, at decidedly different rates. The relatively slow cooling of the 1-ton bulk of slag during the 3-day interval between draw and grinding was much more conductive to crystallinity than was the relatively rapid cooling of the 1-pound laboratory-prepared melt.

As in the case of the near-6-ton incorporation of the quenched by-product slags, there was no significant cumulation of carbonate from like incorporations of the two experimental quenched slags. When the input of Ca was in excess of sorptive capacity of the soil, however, substantial cumulations of $CaCO_3$ came from both of the experimental slags in both soils. It is evident that the infused calcium fluoride accelerated the dissolution of associated silicate content, since the cumulations of $CaCO_3$ from the fluoride-impregnated slag were virtually twice those that developed from the fluoride-free slag.

Effect of cropping upon the carbonatation of various calcium silicate materials

The influence of plant growth upon silicate-to-carbonate conversions was not included in the foregoing comparisons. It would seem probable that the conver-

TABLE 6

Variance in accumulation of CaCO₃ from incorporations of quenched and unquenched slags and wollastonite, in cropped and uncropped Hartsells fine sandy loam

INCORPORATIONS*		CaCO₃ PER 2,000,000 POUNDS OF SOIL AFTER							
Material†	CaCO₃-equivalence	62 days		118 days		232 days		326 days	
		Cropped	Uncropped	Cropped	Uncropped	Cropped	Uncropped	Cropped	Uncropped
	lbs.‡	lbs.	lbs.	lbs.	lbs.	lbs.	lbs.	lbs.	lbs.
Limestone	11,700	3,300	3,600	3,000	2,200	2,600	2,400	2,100	2,800
	35,000	20,300	24,700	20,700	23,800	21,600	18,300	22,900	22,800
Slag, quenched, S-1084									
Unground	11,700	100		600	700	200	200	200	
	35,000	600	900	1,000	300	2,100	400	1,900	1,000
Ground	11,700	500	400	400	100	400	300	100	400
	35,000	10,800	8,900	11,200	9,300	12,400	9,900	12,900	10,900
Slag, unquenched, S-1083									
Ground	11,700	100	600	100	200	200	300	200	100
	35,000	2,600	400	2,700	1,000	2,800	700	3,700	1,000
Wollastonite, S-1027§									
Raw	11,700	100	100	100	100	100	200	100	300
	35,000	100	500	100	400	300	200		100
Fused and unquenched	11,700	200		100	400	100	100		
	35,000	7,200	1,500	8,300	1,300	9,300	2,300	9,600	1,400
Fused and quenched	11,700	200	300	300	300	100	400	400	700
	35,000	10,000	9,000	11,000	9,300	12,400	10,900	10,900	9,900
Experimental slags″, quenched									
Without CaF₂, S-920	11,700		2,800	400	200	200	100		100
	35,000	6,400	5,100	6,100	5,700	6,300	5,800	6,300	5,700
With CaF₂, S-921	11,700	500	600	600	500	200	400	200	800
	35,000	13,000	10,700	12,800	11,700	13,300	10,400	13,100	12,200

* With upper half of soil.
† With the exception of "unground" (10-mesh) slag, all materials were minus 100-mesh.
‡ Basis of 2,000,000 pounds of soil.
§ Contained 1.0 per cent of CaCO₃.
″ Of a mixture of limestone and quartz and Al₂O₃ and Fe₂O₃, in simulation of by-product slag.

TABLE 7

Variance in accumulation of CaCO₃ from incorporations of quenched and unquenched slags and wollastonite, in cropped and uncropped Fullerton silt loam

Material[†]	CaCO₃-equivalence[‡] (lbs.)	$CaCO_3$ PER 2,000,000 POUNDS OF SOIL AFTER							
		62 days Cropped	62 days Uncropped	118 days Cropped	118 days Uncropped	232 days Cropped	232 days Uncropped	326 days Cropped	326 days Uncropped
		lbs.	lbs.	lbs.	lbs.	lbs.	lbs.	lbs.	lbs.
Limestone	11,700	4,600	6,000	3,000	3,700	3,400	3,700	2,800	3,600
	35,000	25,300	23,400	25,900	25,300	25,700	28,400	25,300	27,600
Slag, quenched, S-1084									
Unground	11,700	300	300	900	200	100	400	400	200
	35,000		700	700	200	1,900		2,200	1,900
Ground	11,700	700	400		600	500	400	400	100
	35,000	8,200	8,500	9,600	7,300	9,000	9,500	10,500	9,400
Slag, unquenched, S-1083									
Ground	11,700	100	300	100	400	200		700	
	35,000	1,800	1,000	2,100	800	2,200	800	8,200	1,200
Wollastoniate, S-1027[§]									
Raw	11,700		300	100	400	100		500	
	35,000		800	100	300	300	400	500	600
Fused and unquenched	11,700		200	100	300			200	
	35,000	8,600	3,000	10,800	2,000	12,700	2,600	12,000	3,700
Fused and quenched	11,700	700	300	500	500	200	400	100	500
	35,000	13,900	10,600	12,700	12,800	12,900	14,500	13,100	11,200
Experimental slags″, quenched									
Without CaF₂, S-920	11,700	200	400	800	200	700		100	
	35,000	9,200	9,600	7,700	8,400	8,000	8,900	6,900	8,000
With CaF₂, S-921	11,700	1,300	800	900	800		500	500	700
	35,000	14,100	12,900	14,000	14,500	14,300	16,000	13,500	13,300

* With upper half of soil.

† With the exception of "unground" (10-mesh) slag, all materials were minus 100-mesh.

‡ Basis of 2,000,000 pounds of soil.

§ Contains 1.0 per cent of $CaCO_3$.

″ Of a mixture of limestone and quartz and Al_2O_3 and Fe_2O_3, in simulation of by-product slag.

sion of calcic silicates to $CaCO_3$ would be affected by variations in plant-growth secretions and uptake.   The data of tables 6 and 7 show the periodic cumulations of carbonate from the 16 separate incorporations of silicates in parallel on cropped and fallow soils.   The 36 units that comprised the two series in each soil were sampled simultaneously after each of the four periods, 62, 118, 232, and 326 days, and analyzed by the method of Shaw and MacIntire (13).

In every case, cumulation of carbonate from the near-6-ton incorporation of silicate material was a small fraction of the amount residual from the limestone control.   The successive analyses indicate a progression in slag-derived carbonate content in some of the crop-versus-fallow comparisons, and the reverse
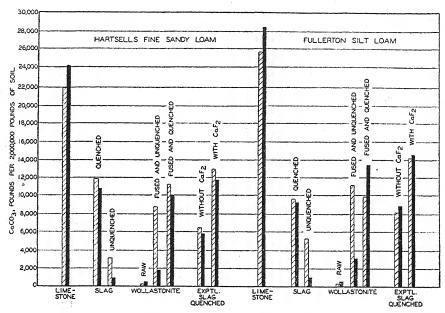
Fig. 1. Variance in the Degree of Carbonatation of 17.5-ton $CaCO_3$-Equivalen
Incorporations of 100-Mesh Calcium Silicate Materials
in Cropped and Uncropped Soils
Solid bars represent cropped soils

tendency in others.   Since 12 of the 16 comparisons on each soil show less than 500 pounds of slag-derived $CaCO_3$ as the respective 4-period means, the results are not conclusive as to whether carbonatation of the near-6-ton incorporations was expedited by root growth.

The carbonate cumulations from the 17.5-ton incorporations of the ground slags, the fused wollastonite, and the experimental slags, were increased somewhat by the cropping of Hartsells fine sandy loam.   This was true also of 13 of the 24 periodic comparisons on Fullerton silt loam, and held likewise for five of the six comparisons as to final occurrences of $CaCO_3$.

In the 32 comparisons for the 17.5-ton rate on each of the soils, the cumulations of carbonate from the quenched materials were greater than those from the un-

quenched materials. The inclusion of CaF_2 in the experimental slag proved accelerative to carbonatation under both cropping and fallow in both soils and at every period.

The means of the 4-period occurrences of carbonate from the 17.5-ton incorporations are graphed in figure 1 to give an overall picture of the disparities between the conversions of the distinctive silicate materials in both soils, under fallow and under cropping.

Supplemented by related results from uncropped potted soils that were subjected to parallel aerations with normal air and with CO_2-free atmosphere, these findings indicate that the CO_2 generated by soil organisms is chiefly responsible for the enhancements in the carbonate content of soils in which the readily hydrolyzable quenched calcium silicate slags are incorporated at rates that admit of residues of $CaCO_3$ from corresponding incorporations of limestone.

Explanatory observations as to variance in degree of carbonatation of calcium silicate materials

In considering the distinctive behavior of the several silicate materials in the soil, it is necessary to recognize the elementary fact that all of the calcic silicates *tend* to undergo hydrolysis, the progress of which is governed by the rapidity of the reaction between the generated hydroxide and the acidic soil components, including CO_2. The hydrolytic reaction is reversible, however, colloidal silica being reactive with solute $Ca(OH)_2$ (12), as well as with $Mg(OH)_2$ additions in the soil (6). When an incorporation of slag is inadequate to satisfy the capacity of a soil to sorb calcium, a major portion of the slag-derived hydroxide apparently reacts directly with contiguous acidoids, although a minor portion may react with CO_2 and form occasional specks of carbonate. Any such specks probably would be of temporary duration, since they would be subject to translocation mechanically and in the dissolved forms indicated by the last two equations. The fate of the incorporated silicates of calcium in the *unleached* potted soils may be accounted for chiefly by transitions indicated by the first four of the following five equations:

$$CaSiO_3 + \text{water} \rightarrow Ca(OH)_2 + SiO_2 \cdot nH_2O$$
$$Ca(OH)_2 + H_2\text{-complex} \rightarrow Ca\text{-complex} + 2H_2O$$
$$Ca(OH)_2 + CO_2 \longrightarrow CaCO_3 + H_2O$$
$$Ca(OH)_2 \text{ (or } CaCO_3) + 2HNO_3 \rightarrow Ca(NO_3)_2 + 2H_2O \text{ (or } CO_2)$$
$$Ca(OH)_2 + 2CO_2 + \text{water} \rightarrow CaH_2(CO_3)_2 + H_2O$$

Because of the acidoid fixation of the derivative hydroxide, enhancement of the carbonate content of a moderately slagged soil will be so limited and variable that the progress of the disintegration of the slag would not be revealed by sequential determinations of fixed CO_2. Hence, to determine differences in the speed and extent of carbonatation of incorporated silicates, it is essential to introduce the silicate materials at rates that provide calcium beyond the fixation capacity of the soil.

In meeting the foregoing requirement, however, unforseen variables arise because of the inherent characteristics of the different calcic materials. The accounting for the unsorbed fraction of the Ca of the heavy incorporations of quenched slag in unleached soil does not rest solely with the formation of $CaCO_3$ and other biochemical end-products. On the basis of periodic determinations on the pH of the potted soils and unpublished lysimeter findings over a 5-year period, it was evident that heavy incorporations of ground quenched slag induced immediate chemical and biochemical phenomena similar to those induced by comparable incorporations of burnt lime and hydrated lime. Reactions other than those indicated by the equations may generate certain distinctive temporary combinations that embrace oxides of Al and Fe. During the progressive disintegrations of the heavy incorporations of slag, the pH in the soil system is at the high level conducive to the development of the tricalcium aluminates and ferrates and their respective ternary sequences, $3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 33H_2O$ and $3CaO \cdot F_2O_3 \cdot 3CaSO_4 \cdot nH_2O$, which develop when hydrated oxides of aluminum and iron are suspended in an aqueous system alkalinized by $Ca(OH)_2$ and containing $CaSO_4$ (4, 5, 7). Hence, so long as requisite alkalinity and concomitant paucity of CO_2 prevail in heavily slagged moist soil systems, the Ca of such generated ternary compounds will not undergo integration to the carbonate form. When the generated hydroxide is diminished through sorption by the soil or by carbonatation, and in the absence of an excess of solute $CaSO_4$, the exposed unstable ternary solids undergo disintegration and yield component $CaCO_3$, Al_2O_4, and $CaSO_4$. On the other hand, no equivalent quantity of $CaCO_3$ will come soon from a slag's content of gehlenite, or other strongly resistant Ca-Al-SiO_2 components, although the resistant combinations may undergo carbonatation ultimately. Hence, although progression in the $CaCO_3$ content of soils slagged beyond their capacity to sorb Ca will serve to demonstrate the activity of a given slag, such progression is not the sole index as to the disintegration of the excess of the incorporated slag over a given period.

SUMMARY AND CONCLUSIONS

The relatively new type of "glassy" calcium silicate slag that comes from electric phosphate-reduction furnaces is being used extensively in lieu of limestone. Its reactivity in soils, in contradistinction to the stabilty of crystalline silicate of calcium, is reported in this paper.

Virtually all of the Ca of a 5-ton incorporation of quenched slag was sorbed by a Montevallo silt loam, without appreciable cumulation of $CaCO_3$ during the growth of nine successive crops. With increase in rate and with decrease in particle size, substantial cumulations of carbonate came from heavier incorporations and from the fines of quenched slag; but, invariably, the cumulations were less than the residues of limestone in the controls.

At a 39-ton rate, neither wollastonite nor its calcines underwent conversion to carbonate in cropped Hartsells fine sandy loam, whereas corresponding incorporation of quenched slag registered a 15-ton gain in $CaCO_3$.

Substantial and proportional cumulations of $CaCO_3$ came from three quenched

slags, under three crops, in two soils that were slagged at rates beyond sorptive capacity, the carbonatation having occurred chiefly during the growth of the initial crop, whereas no increase in carbonate content came from the parallel incorporations of wollastonite.

The cumulations of $CaCO_3$ from quenched "glassy" slag were far more extensive than those from its unquenched crystalline companion slag, under five successive crops in each of two soils. A similar disparity in carbonate cumulations was registered by the quenched and unquenched portions of a laboratory melt of wollastonite.

Carbonate cumulations from incorporations of a quenched experimental slag that contained calcium fluoride ($CaO\text{-}Al_2O_3\text{-}F_2O_3\text{-}SiO_2\text{-}CaF_2$) were twice as great as the cumulations from companion incorporations of a slag devoid of that fluoride.

Accelerated carbonatation of the quenched slags and quenched melts of wollastonite may have been induced by cropping; in the case of the less active unquenched silicate materials, however, the accelerative effect was substantial and conclusive.
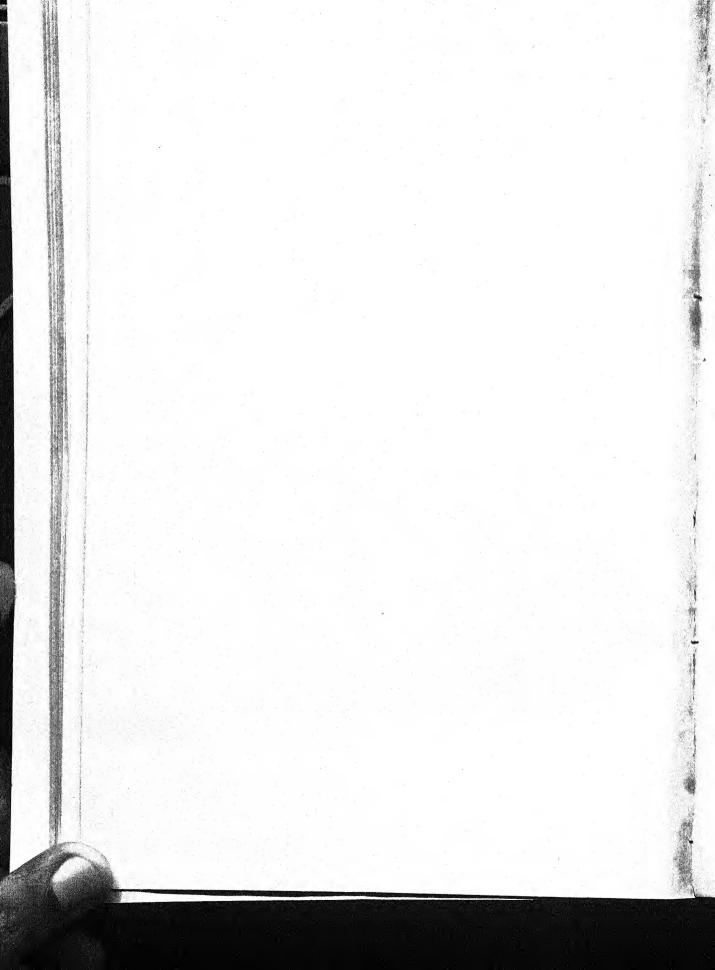
The processes responsible for the silicate transitions are discussed, in accounting for the disparate reactivities of the "glassy" and crystalline forms in the soils.

When the foregoing observations are integrated with the results obtained when slagged soils were aerated with normal air and with CO_2-free atmosphere, it appears that the CO_2 of the carbonate cumulations in the slagged soils is attributable to bacterial activations in the soil, rather than to influent atmosphere.

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THE LAWS OF SOIL COLLOIDAL BEHAVIOR: XXIV. DONNAN EQUILIBRIA IN SOIL FORMATION

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In a previous paper in this series Mattson and Wiklander (10) were able to account for the amphoteric reactions of soils: for the intersections of the titration curves obtained in various salt solutions and for the relative position of the equi-ionic points and the point of exchange neutrality, on the basis of the valence effect in the Donnan equilibrium. Later Mattson (12), experimenting with a common bath sponge, could show that the exchange between monovalent, divalent, and trivalent cations, resulting from a dilution of the system, is qualitatively as required for ideal Donnan systems.

This work was based on the theoretical relationship between the valence of the ions and their distribution in a Donnan system at different dilutions of the "outside" solution. But the distribution of ions of different valence in a Donnan system must be governed by the *relative* dilution of the outside solution, and depends therefore on the concentration of the "inside" solution as well.

This recognition, together with a little reflection, leads to the following deductions:

1. Soils having a low cation-exchange capacity, that is, soils which are weak acidoids, such as red earths and laterites, should, other things being equal, contain a higher proportion of exchangeable monovalent cations (Na and K as compared to Ca and Mg) than soils having a high exchange capacity. The former soils possess a lower micellar-ion concentration (a more dilute inside solution) and should adsorb the monovalent ions relatively better than the latter.

2. The more unsaturated a soil, the greater should be the proportion of exchangeable monovalent cations. The undissociated acidoid does not participate in the Donnan equilibrium. A highly unsaturated soil has, therefore, a greatly reduced micellar-ion concentration and should adsorb the monovalent cations relatively better than the saturated soils.

3. Among the leached soils the proportion of alkali cations should therefore be greatest in the highly unsaturated soils possessing weak acidoid properties, whereas the proportion of the alkaline earth cations should be greatest in the slightly leached, saturated soils possessing a high exchange capacity.

The present paper deals with a theoretical discussion and experimental evidence in support of these deductions.

DONNAN EQUILIBRIA

The equilibrium distribution of monovalent ions, for example those of KCl, between the "inside" and the "outside" solution of a Donnan system containing a negative colloid (an acidoid) may be expressed by the equation

$$x_{Cl} \cdot x_K = y_{Cl}(y_K + z_K) \qquad (A)$$

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where x = the activity of the anions and cations of the free salt in the outside solution, y = their activity in the inside solution, and z = the activity of the cations in combination with the acidoid.

For the $CaCl_2$ the distribution would be

$$x^2_{Cl}\text{-}x_{Ca} = y^2_{Cl}(y_{Ca} + z_{Ca}) \qquad (B)$$

This is the principle of a constant-ion activity product which we postulate as a thermodynamic necessity.

The relative activities of the ions in the inside and outside solutions may, for our purpose, be formulated as follows:

$$\frac{x_{Cl}}{y_{Cl}} = \frac{y_H + z_H}{x_H} = \frac{y_K + z_K}{x_K} = \frac{\sqrt{y_{Ca} + z_{Ca}}}{\sqrt{x_{Ca}}} \qquad (C)$$

If the activity coefficients of the ions were the same in both phases, as in an ideal system, the equation would express the relative concentrations as well. But the relationship is apparently never so simple in the soil, for it is a common experience that the displacing power of the cations in equal concentrations is always, for the monovalent

$$K^+ > Na^+,$$

and for the divalent

$$Ca^{++} > Mg^{++}$$

This would mean that in the inside solution the order of activity of the single ions is the reverse:

$$Na^+ > K^+ \quad \text{and} \quad Mg^{++} > Ca^{++},$$

which is the same as the order of hydration.

The less hydrated an ion the closer it will get to the surface ions and the greater, therefore, will be its polarizing effect on the surface ions.

The interionic attraction between the anions on the surface and the cations in the ionic atmosphere must, therefore, be assumed to suppress the activity coefficient of the K ions more than that of the Na, and of the Ca more than that of the Mg ions. In accordance with the concept of Bjerrum we must conclude that the degree of association is greater for K than for Na ions and, again, greater for Ca than for Mg ions. This conclusion is supported by the electrokinetic and colloidal behavior of sols and gels saturated with these ions.

The K and Ca ions reduce the charge and the stability of the sols and the swelling of the gels more powerfully than do the Na and Mg ions respectively.

The H ions are usually looked upon as being only slightly dissociated by the solid surface, that is, the soil acidoids are assumed to be like weak acids. Since the crystal lattice is made up of ions, not molecules, and since the surface layer of ions in the lattice must possess a residual charge and, therefore, a certain activity, the word "undissociated" loses some of its old significance. Whether a "slightly dissociated" compound is formed or whether the exchangeable ion be-

comes "highly associated" with the ions on the surface, the effect will be the same: a low activity of that ion in the inside solution and a strong displacing power, all in agreement with the Donnan equation.

An ion may enter as a constituent part of a crystal lattice and thus suffer a great suppression of its activity. This tendency appears to be especially great for the Mg and K ions which generally occur largely as nonexchangeable ions in the secondary clay minerals (8).

The quantitative relationship between concentration and activity in the colloidal phase in a real Donnan system is still very obscure. In a recent analysis of the problem Davis (3) examined the ion distribution in a Na-bentonite system. His results are in line with the early findings of Mattson (9), who reported the apparent dissociation of Na-bentonite to be lowest in the most dilute solutions of NaCl. Davis calculated the activity coefficient of NaCl in the suspension and found it to be lowest in the most dilute solutions of the salt. In concentrated solutions the relative suppression of the activity coefficient in the suspension was very moderate. The conclusion would seem to be that the higher the charge of the particles, the more powerful the interionic attraction and the lower, therefore, the activity coefficient of the ions.

The soil might diverge considerably from an ideal Donnan system, but for the common ions, and within certain limits of their concentration, the divergence may be assumed to be regular and orderly. We would therefore not expect the valence effect, which is very great, to be eclipsed by a divergence between concentration and activity, except in cases of specific affinity between ion and colloid. A quantitative application of the Donnan equilibrium to the soil is not now realizable, but if we can apply the theory semiquantitatively, in terms of concentration, there is much to be gained for soil science. Let us now see what the implications are.

From the square-root relationship in equation (C) it follows that a relatively concentrated micellar solution or a relatively dilute outside solution would favor the adsorption of divalent cations and increase their relative displacing power, whereas a relatively dilute micellar solution or a relatively concentrated outside solution would favor the adsorption of monovalent cations and increase their relative displacing power.

This means, first, that a soil having a low micellar-ion concentration (a low and diffuse acidoid content) must contain a higher proportion of exchangeable monovalent cations than a soil having a high micellar-ion concentration (a high and dense acidoid content), when the two soils are in equilibrium with the same solution, and second, that one and the same soil must contain a higher proportion of exchangeable monovalent cations when, in equilibrium with an acid solution, it is only slightly saturated with metal cations than when, in equilibrium with a neutral solution of otherwise identical composition, it is saturated with metal cations and possesses a high micellar-ion concentration.

When the outside ion activity approaches that of the micellar solution, that is, when the quotients in equations (C) approach unity, the valence effect will vanish and the displacing power of monovalent and divalent cations will be

about equal. This condition will be attained at an outside activity which is lower, the lower the micellar-ion activity. The word "concentrated" becomes here a relative term, for a solution which is concentrated with respect to a soil having a low micellar-ion concentration may be relatively dilute with respect to a soil which possesses a concentrated micellar solution.

The theoretical distribution of ions in an ideal Donnan system is shown in table 162 for various values of y_{M^+} in terms of z_{M^+}. From the distribution ratios of the monovalent, and divalent ions the percentage composition in the inside solution has been calculated for the case $x_{M^+} = x_{M^{++}}$. The method of calculation is the following.

From equation (A)[1] it follows that

$$\frac{y_{M^+} + z_{M^+}}{x_{M^+}} = \frac{x_{Cl^-}}{y_{Cl^-}} = \frac{\sqrt{y_{M^+}(y_{M^+} + z_{M^+})}}{y_{M^+}} = \sqrt{\frac{y_{M^+} + z_{M^+}}{y_{M^+}}} = \sqrt{1 + \frac{z_{M^+}}{y_{M^+}}} \qquad (D)$$

TABLE 162

Theoretical, relative distribution of monovalent and divalent cations in an ideal Donnan system

WHEN $y_{M^+} =$	$z_{M^+}/10000$	$z_{M^+}/1000$	$z_{M^+}/100$	$z_{M^+}/10$	z_{M^+}	$10 z_{M^+}$
$\dfrac{y_{M^+} + z_{M^+}}{x_{M^+}} =$	100.005	31.639	10.050	3.317	1.414	1.050
$\dfrac{y_{M^{++}} + z_{M^{++}}}{x_{M^{++}}} =$	10001.00	1001.00	101.00	11.00	2.00	1.10
When $x_{M^+} = x_{M^{++}}$ $y_{M^+} + z_{M^+}$ (%) =	0.99	3.06	9.05	23.15	41.42	48.78
$y_{M^{++}} + z_{M^{++}}$ (%) =	99.01	96.94	90.95	76.85	58.58	51.22

By substituting the values in the top row in table 162 for z_{M^+}/y_{M^+} in the last expression, we get the corresponding distribution of the monovalent ions shown in the second row of the table.

From equations (C) and (D)

$$\frac{\sqrt{y_{M^{++}} + z_{M^{++}}}}{\sqrt{x_{M^{++}}}} = \frac{y_{M^+} + z_{M^+}}{x_{M^+}} = \sqrt{1 + \frac{z_{M^+}}{y_{M^+}}} \qquad (E)$$

Hence

$$\frac{y_{M^{++}} + z_{M^{++}}}{x_{M^{++}}} = 1 + \frac{z_{M^+}}{y_{M^+}} \qquad (F)$$

We thus get the corresponding distribution of the divalent ions shown in the third row of the table.

[1] Since $x_K = x_{Cl}$ and $y_K = y_{Cl}$, equation (A) may be written $x^2 = y(y + z)$, from which we get $\dfrac{y + z}{x} = \dfrac{x}{y} = \dfrac{\sqrt{y(y + z)}}{y}$ etc. as in (D).

The percentage composition of the inside solution in equilibrium with an outside solution in which $x_{M^+} = x_{M^{++}}$ is shown in the last two rows of the table. The relationships are shown graphically in figure 119.

The calculations show, first, that in dilute solutions, in which y is small compared to z, the displacing power of the divalent ions should be much greater than that of the monovalent ions, whereas in concentrated solutions, in which y is relatively large, the displacing power of the monovalent ions should approach that of the divalent, and second, that the relative displacing power of the monovalent ions at a given concentration should increase with a decrease in the value of z.
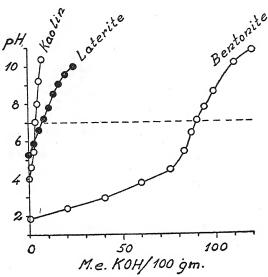
FIG. 118. TITRATION BY KOH, IN N KCl SOLUTION, OF ELECTRODIALYZED BENTONITE, KAOLIN, AND LATERITE

EXPERIMENTAL

The materials used include a Wyoming bentonite ("volclay"), a commercial sample of kaolin, and the Las Mesas laterite (horizon II = 13–23 inches) from Puerto Rico, described by Mattson and Wiklander. Figure 118 shows the titration curves of the electrodialyzed materials.

The bentonite, which contained CaSO₄, was first washed for several weeks with 0.05 N HCl and water by decantation in a glass cylinder of 40-liter capacity. It was then electrodialyzed for over 2 weeks, at the end of which it was free from Ca and SO₄ ions. The kaolin and laterite were electrodialyzed directly.

Titration with KOH in N KCl solution showed the base-binding capacities at pH 7 to be about 3.5, 7.5, and 90 m.e. per 100 gm. for kaolin, laterite, and bentonite respectively. [At pH 6 the capacity was 3 m.e. per 100 gm. for both kaolin and laterite (cf. fig. 118).] We have, therefore, good reason to assume

that, at the same base status, the micellar-ion concentration (z) will be a good deal lower in kaolin and laterite than in bentonite. (A high z concentration might be associated with a low exchange capacity when an acidoid having a high capacity is diluted by an admixture of chemically indifferent particles.)

The experiment was conducted as shown in table 163. The NH$_4$ and Ca ions were added in equivalent proportions. By using a minimum amount of adsorbent (2 gm. bentonite and 40 gm. kaolin and laterite) and increasing the

TABLE 163

Adsorption of NH$_4$ and Ca ions by electrodialyzed bentonite, kaolin, and laterite from solution containing equivalent quantities of NH$_4$Cl and CaCl$_2$

Bentonite = 2 gm., kaolin = 40 gm., laterite = 40 gm.   Each system received 1 m.e. NH$_4$OH and 1 m.e. Ca(OH)$_2$

MATERIAL	VOLUME	CONCENTRATION NH$_4$Cl + CaCl$_2$	EXCHANGEABLE NH$_4$	EXCHANGEABLE Ca	EXCHANGEABLE NH$_4$ + Ca	$\dfrac{Ca}{NH_4}$
	liters	N	*m.e./100 gm.*	*m.e./100 gm.*	*m.e./100 gm.*	
A: Exchangeable NH$_4$ and Ca after washing out the chlorides						
Bentonite..	40.0	0.001	3.53	74.30	77.83	21.1
	40.0	0.01	6.29	68.91	75.20	10.9 [8.4]*
	4.0	0.1	15.59	60.55	76.14	3.9 [2.3]
	0.4	1.0	40.60	55.39	95.99	1.4
Kaolin.....	40.0	0.001	0.36	2.84	3.20	8.0
	40.0	0.01	0.57	2.18	2.75	3.9
	4.0	0.1	1.02	2.14	3.16	2.1
	0.4	1.0	1.30	2.65	3.95	2.0
Laterite....	40.0	0.001	0.29	1.79	2.08	6.2
	40.0	0.01	0.41	1.34	1.75	3.3 [3.3]
	4.0	0.1	0.45	1.41	1.86	3.2 [1.6]
	0.4	1.0	0.38	1.28	1.66	3.4
B: Exchangeable NH$_4$ and Ca without washing (chlorides subtracted)						
Bentonite..	10.0	0.01	7.83	65.97	73.80	8.4
	1.0	0.1	26.06	59.25	85.31	2.3
Laterite....	10.0	0.01	0.38	1.26	1.64	3.3
	1.0	0.1	0.71	1.16	1.87	1.6

* Bracketed figures, exchangeable NH$_4$ and Ca without washing (chlorides subtracted).

volumes up to 40 liters we could go down to a concentration of NH$_4$Cl + CaCl$_2$ = 0.001 N without seriously changing the original 1:1 proportion of the salts by the exchange reaction.

The addition of 1 m.e. NH$_4$OH and 1 m.e. Ca(OH)$_2$ to the solutions (before the adsorbents were added) brought the pH of the systems to between 6.02 (laterite) and 6.81 (bentonite).

The systems containing 40 liters were kept in glass cylinders and were agitated for 30 hours by a current of outdoor air. The other systems were shaken in the

machine for 30 hours in closed containers. The suspensions were then allowed to settle, after which the supernatant solution was decanted and the sediments were transferred to filter funnels and washed free of chlorides. The adsorbed NH_4 and Ca ions were then replaced with a 0.05 N HCl solution and determined in the usual manner. The results are shown in table 163 A.

It was realized that this method of washing the samples free of chlorides is wrong in principle. For if the soil is a Donnan system, as we had every reason to believe from our previous work, then the progressive dilution during the washing would cause the Ca ions of the free salt to displace some of the adsorbed NH_4 ions. This effect would be greater the more concentrated the system and can be neglected only in the most dilute system, in which the amount of chloride in the drained samples would be very small (a few cubic centimeters 0.001 N). But since this is the method most commonly used, we desired to try it and compare the result with that of a more accurate method.

It is to be noted in table 163 A that the large (40 gm.) samples of kaolin and laterite, which imbibed the greatest amount of salt solution, show evidence of the aforementioned effect, in that the Ca/NH_4 ratios do not continue to decrease in the concentrated systems. The washing has obviously led to the readjustment demanded by the Donnan distribution.

To determine exactly the equilibrium composition of the exchangeable cations is virtually impossible. To replace the ions directly, without washing, with dilute HNO_3 and then determine the Cl ions in an aliquot of the filtrate, and subtract these as free chloride, is perhaps the first method which might suggest itself. But laterite and kaolin adsorb Cl ions even at relatively high pH. To consider the Cl ions as free chlorides would, in such cases, yield too low values for the exchangeable cations.

The results given in table 163 B were obtained as follows: The funnel containing the drained sample was weighed, the ions were displaced with 0.05 N HCl, and the funnel with its contents was dried at 105°C. and again weighed. From the loss in weight and from the analysis of a weighed aliquot of the supernatant liquid the free salts present in the moist samples were estimated and corrected for. Since the supernatant solution must contain more free salt than the solution in the moist sample ($x > y$) this correction must yield somewhat low values for the exchangeable cations, but, up to a concentration of 0.1 N, the ratios Ca/NH_4 should not be seriously affected.

It is obvious that, by the B method, the Ca/NH_4 ratio in the laterite decreases from 3.3 to 1.6 as the salt concentration increases from 0.01 to 0.1 N. The B ratios for bentonite show a decrease in both concentrations. All of this indicates that the washing (in A) has led to a replacement of NH_4 by Ca.

In Figure 119 is plotted the percentage composition (m.e. NH_4 + Ca = 100) of the exchangeable cations in bentonite and laterite against the logarithm of the sum of the (initial) concentration of the NH_4 and Ca ions in the solution as given in table 163 B and for 0.001 N in table 163 A.

The experiment establishes the fact that the relative displacing power of the monovalent ions, which is very low in dilute solutions, increases rapidly with increasing concentration, and further, that at a given salt concentration, the

monovalent ions are adsorved relatively much better by kaolin and laterite, which possess a lower exchange capacity and presumably a lower micellar-ion activity, than by bentonite, which has a high capacity and which must possess
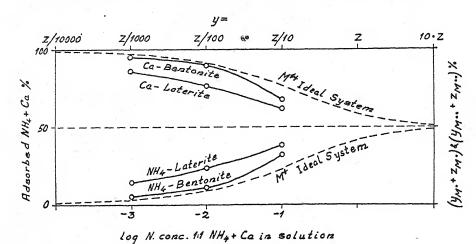
FIG. 119. PERCENTAGE OF MONOVALENT AND DIVALENT IONS IN THE "INSIDE" SOLUTION OF AN IDEAL DONNAN SYSTEM AT DIFFERENT y VALUES, AND THE PERCENTAGE OF EXCANGEABLE NH_4 AND Ca IONS IN SOILS WITH HIGH (BENTONITE) AND WITH LOW (LATERITE) EXCHANGE CAPACITY AT DIFFERENT SALT CONCENTRATIONS

Compare tables 162 and 163

TABLE 164

Adsorption of NH_4 *and* Ca *ions by electrodialyzed bentonite, at various degrees of base saturation, from solutions containing equivalent quantities of* NH_4Cl *and* $CaCl_2$

NH_4Cl and $CaCl_2$ concentration each = 0.005 N; volume = 10 liters

BEN- TONITE	BASE OR ACID ADDED	pH	EXCHANGE- ABLE NH_4	EXCHANGE- ABLE Ca	EXCHANGE- ABLE NH_4 + Ca	$\dfrac{Ca}{NH_4}$
gm.	m.e.		m.e./100 gm.	m.e./100 gm.	m.e./100 gm.	
2	1.0 NH_4OH + 1.0 $Ca(OH)_2$	6.81	7.83	65.97	73.80	8.4
5	1.25 NH_4OH + 1.25 $Ca(OH)_2$	4.75	6.71	53.65	60.36	7.9
5	None	3.80	5.91	45.10	51.01	7.5
5	10 HCl	3.00	4.86	32.80	37.66	6.7
5	100 HCl	2.05	4.17	24.10	28.27	5.9
5	300 HCl	1.51	4.84	19.82	24.66	4.1
5	1000 HCl	1.10	4.78	10.79	15.57	2.3

a high micellar-ion activity, all as demanded by the "mass law" for Donnan systems (compare the theoretical curve in figure 119).

We shall now see how this law operates in a series of systems containing the same adsorbent (bentonite) but in which the micellar-ion concentration is progressively decreased by a gradual substitution of the cations by H ions.

Table 164 gives the results obtained by the method of subtracting the chlorides

(as in table 163 B). The Ca/NH_4 ratios decrease from 8.4 to 2.3 as the base saturation is reduced from 73.8 to 15.6 m.e. per 100 gm. The first and the last ratios in the table represent the average of duplicate analyses which showed a good agreement.

The results in table 164 are, however, not so satisfactory as might be desired. It does not seem probable that the exchangeable NH_4 should remain virtually constant over the entire range of pH from 3.0 to 1.1. The method is apparently not sufficiently accurate for small amounts of ions. It is very difficult to leach 5 gm. of the very voluminous and impervious bentonite gel, the process sometimes requiring several weeks. Though the trend in the Ca/NH_4 ratios leaves no doubt that our prediction—that the proportion of the monovalent cations in the exchange complex should increase with decreasing saturation—is fulfilled, we were not satisfied with the results and decided to try a third method. For this work a new batch of purified bentonite had to be prepared.

TABLE 165

Adsorption of NH_4 and Ca ions by electrodialyzed bentonite, at various degrees of base saturation, from approximately 0.01 N solutions of NH_4Cl and $CaCl_2$

5 gm. bentonite in 200 cc. solution

NUM-BER	CHEMICALS ADDED					pH	EQUILIBRIUM CONCENTRATION		EX-CHANGE-ABLE NH4	EX-CHANGE-ABLE Ca	EX-CHANGE-ABLE NH4 + Ca	$\frac{Ca}{NH_4}$
	NH_4OH	Ca (OH)$_2$	HCl	NH_4Cl	$CaCl_2$		NH_4	Ca				
	m.e.	m.e.	m.e.	m.e.	m.e.		N	N	m.e./100 gm.	m.e./100 gm.	m.e./100 gm.	
1	.536	3.221		2.00	2.00	4.94	.01005	.01004	10.52	64.26	74.78	6.1
2	.206	0.767		2.174	2.814	2.51	.01017	.01031	6.92	30.40	37.32	4.4
3				2.310	3.210	2.19	.00997	.00938	6.32	26.68	33.00	4.2
4			20.00	2.246	2.468	1.08	.00995	.00963	5.12	10.84	15.96	2.1

The method, the results of which are given in table 165, consists in shaking 5 gm. of bentonite for 3 days with 200 cc. of solution and, by means of trials and adjustments, working toward an equilibrium concentration of approximately 0.01 N with respect to both NH_4 and Ca ions. After equilibrium, the suspension is filtered and the filtrate, which contains a suitable amount of NH_4 and Ca ions, is analyzed. There is here no leaching, the sediment on the filter being discarded. The accuracy of the analysis was increased by preparing a large volume (500 cc.) of the original solution. From this solution 200 cc. was measured out for the bentonite equilibrium and the remainder was used for a determination of the NH_4 and Ca concentration in the original solution. After each experiment a new solution was made up in which the deficiencies were compensated. This entails a good deal of analytical work but the method is otherwise very simple.

It should be added that 5 gm. of the bentonite when shaken with 200 cc. 0.1 N HCl yielded at most a trace of Ca.

After three trials and adjustments the results shown in table 165 were ob-

tained.   The equilibrium concentration in numbers 3 and 4 is still a little too low with respect to the Ca ions, but for the second time the purified bentonite had been used up, and the experiment was discontinued.

The Ca/NH$_4$ ratios decrease from 6.1 to 2.1 as the base saturation is reduced from 74.78 to 15.96 m.e. per 100 gm.   While the exchangeable Ca ions decrease from 64.26 to 10.84 m.e. per 100 gm. the NH$_4$ ions decrease only from 10.52 to 5.12 m.e.   The experiment thus confirms our theoretical conclusions.

APPLICATION TO SOIL CONDITIONS

It has been shown that a dilution of the "outside" solution (containing monovalent and divalent cations) leads to a replacement of monovalent by divalent cations and an increase in the proportion of the latter in the exchange complex, whereas a "dilution" of the "inside" or micellar solution (brought about by lowering the base saturation) has the opposite effect and leads to an increase in the proportion of monovalent ions in the exchange complex.

Thus if a saturated soil is leached with an acid solution whose concentration of metal cations is equal to that of the solution originally in equilibrium with the soil, relatively more divalent than monovalent cations will be removed from the soil.   The ratio M^{++}/M$^+$ in the exchange complex will decrease as the solution becomes more acid.   If, for example, bentonite saturated with 10.52 m.e. NH$_4$ and 64.26 m.e. Ca per 100 gm. (system 1, table 165) is leached with a solution which is a little over 0.1 N (0.1 N plus exchange acidity in system 4, table 165) with respect to HCl, 0.00995 N NH$_4$Cl, and 0.00963 N CaCl$_2$, the bentonite eventually will contain 5.12 m.e. NH$_4$ and 10.84 m.e. Ca in the exchangeable form.   The leaching will have resulted in a loss of 83.13 per cent of the exchangeable Ca and only 51.34 per cent of the exchangeable NH$_4$.   The acid leaching will, other things being equal, result in an increase in the M^{++}/M$^+$ ratio of exchangeable ions.

But in nature the other things do not remain equal.   The soil solution may become more dilute or it may become more concentrated.   In the former case, the M^{++}/M$^+$ ratio of the exchangeable cations must increase whereas in the latter case it must decrease (see table 163).   If, for example, water is added to system 1 in table 165 the outside solution will be diluted, with the result that Ca ions will displace some of the exchangeable NH$_4$ ions.   If, on the other hand, an acid is added to the system, both NH$_4$ and Ca ions will be displaced by H ions and their concentration in the outside solution will increase whereas their concentration in the micellar solution will decrease.   As a result, relatively more Ca than NH$_4$ will be displaced by the H ions.

Leaching tends to dilute the soil solution.   But leaching is, under natural conditions, accompanied by an increase in acidity, and an increase in free acidity must result in a lowering of the quotient $y_H + z_H/x_H$.   This would mean that the dilution of the micellar solution proceeds relatively faster than the dilution of the outside solution.   We would therefore expect base-unsaturated soils to possess a higher proportion of exchangeable monovalent ions than saturated soils.   This proportion should, at a given base status, be higher the more moder-

ate the leaching, that is, the less dilute the soil solution. At a given acidity it ought to be higher, in general, the higher the isoelectric point, that is, the weaker the acidoid of the soil complex.

From the point of view of Donnan equilibria soils might be divided into three major groups:

1. Supersaturated, saline soils which possess a high concentration of monovalent cations but, because of the low solubility of $CaSO_4$, $CaCO_3$, and $MgCO_3$, a relatively low concentration of divalent cations in the soil solution. These soils are known to contain a high proportion of exchangeable K and Na ions. When such soils are subjected to leaching there will be a displacement of monovalent by divalent cations (dilution effect). The extent of this displacement will depend upon the presence or absence of undissolved $CaSO_4$ and $CaCO_3$. In their presence the displacement will proceed very far because the greater the dilution of the soil solution the greater will be the relative displacing power of the divalent ions (the concentration of which will be virtually unaffected by the leaching as long as the undissolved reserve lasts). In the absence of the slightly soluble alkaline earth salts the leaching must lead to the formation of solonetz and solodi soils.

2. Saturated, slightly leached soils such as the chernozem. In these soils, in which there is no accumulation of the highly soluble alkali salts, the displacement of the monovalent by the divalent cations must proceed further than in any other soil group. The Ca + Mg/K + Na ratio attains here a maximum, which should be higher the higher the exchange capacity of the soil. If such soils are leached (degraded), resulting in a displacement of the metal cations by H ions, the divalent cations will be displaced at a higher rate than the monovalent, and the Ca + Mg/K + Na ratio will decrease with the progressive decrease in saturation, leading ultimately to the formation of the next group of soils.

3. Unsaturated, strongly leached soils such as the podzols, red earths, and laterites. The Ca + Mg/K + Na ratio will approach a minimum and should, at a given pH, be lower the weaker the acidoid. It should therefore be lower in the mineral soil than in the humus layer, and among mineral soils it should be lower the higher the isoelectric point of the exchange complex.

Evidence in support of these deductions is not lacking. Thus the equivalent ratios of exchangeable Ca + Mg/K + Na calculated from the data of Hissink (4) and of Kelley and Brown (6) have the following values:

25 Dutch clay soils	11.5
7 Neutral soils (some alkaline), California	7.3
5 Acid soils from different parts of the United States	3.3

The Dutch soils contained an average of 38.3 m.e., the neutral soils 30.3 m.e., and the acid soils 3.9 m.e. exchangeable bases per 100 gm. Obviously, the highly unsaturated acid soils show a much higher proportion of monovalent cations.

Joffe (5) cites Tyurin's data on a chernozem showing a Ca + Mg/K + Na ratio of 81.8 in the 2–14-cm. layer and of 71.1 in the 20–35-cm. layer. Joffe also gives the composition of the exchangeable bases in some Hungarian bad alkali soils (after Sigmond), which yield Ca + Mg/K + Na ratios as low as 0.37.

Thus a high salt concentration or a low base saturation is found to be associated with low Ca + Mg/K + Na ratios of exchangeable bases, whereas the saturated but slightly leached chernozem yields high ratios, all in qualitative agreement with the Donnan equilibrium.

Further evidence is found in the systematic work of Albrecht (1), who studied

FIG. 120. *A*, THE pH; *B*, THE DISTRIBUTION OF EXCHANGEABLE Ca (IN M.E. PER 100 GM. SOIL); AND *C*, THE Ca/K RATIOS OF EXCHANGEABLE IONS IN THE UNDEN HYDROLOGIC PODZOL PROFILE SERIES

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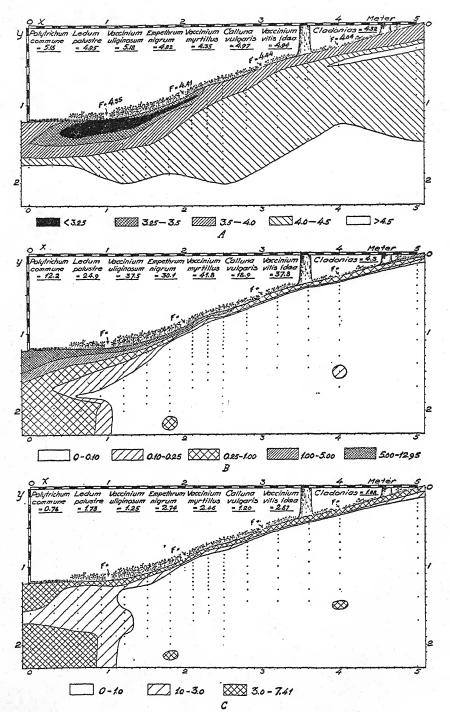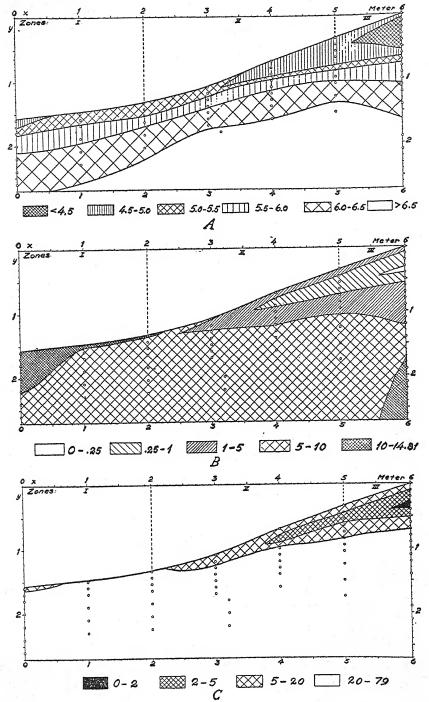Fig. 121. *A*, the pH; *B*, the Distribution of Exchangeable Ca (in m.e. per 100 gm. Soil); and *C*, the Ca/K Ratios of Exchangeable Ions in the Dala Hydrologic Brown Earth Profile Series

four loessial profiles of silt loam in different locations (from Iowa to Mississippi) extending through rainfall increase from 27 to 55 inches, and a temperature increase from 8.72 to 17.66°C.   Arranged in the order of increasing degree of development of the soils (from low to high rainfall) Albrecht reports the following figures for the B horizon:

Exchange capacity, *m.e./100 gm*.................................. 73, 66, 50, 44
SiO_2/M_2O_3.. 5.06, 4.03, 3.24, 2.56
Ca/K (exchangeable)... 132.8, 33.0, 24.2, 15.8

Albrecht does not give the pH or the saturation of the soils.   But from his data it is safe to assume a progressive decrease in these variables in the direction of increasing rainfall.   The relationship would then be the same as that found by our experiment in table 164.

In a number of papers on the pedography of hydrologic soil series Mattson and his associates (2, 7, 11, 14, 15, 16) have studied the distribution of various elements from the "wet" to the "dry" end of such series.   The results are presented in the form of pedographic charts constructed on the pattern of a coordinate system in which the position of each sample is given by its distance from the origin on the x and y axes.   Each dot on the charts represents a sample.

Figures 120 and 121 each reproduce three such charts.   Figure 120 *A*, *B*, and *C* show the pH, the distribution of exchangeable Ca (m.e./100 gm.), and the Ca/K equivalence ratios of exchangeable ions in the Unden podzol profile series respectively.   Figure 121 *A*, *B*, and *C* show the same thing in the Dala brown earth profile series.

The most remarkable thing in connection with our present study is the fact that the Ca/K ratios decrease with a decrease in the base saturation, as expressed by the Ca content, in both series of soil profiles.   This is exactly what we found in our laboratory experiments (tables 164 and 165) and what the Donnan theory demands.

The fact that the Ca-distribution charts closely resemble the Ca/K charts shows that the leaching takes place chiefly at the expense of the divalent Ca ions, which are displaced by H ions at a higher rate than the monovalent K ions.   This result is the same as that reported by Albrecht for his loessial series of soils.

In the Dala brown earth there is a recurrence, in the B_1 horizon at the dry end, of a wedge showing maxima or minima with respect to several variables.   Thus, besides the three variables here shown, we found minima for exchangeable Mg and maxima for acid oxalate-soluble Al, Fe, and Ti and for exchange alkalinity, all in the form of a characteristic wedge in the same place.   The pronounced drop in the Ca/K ratios in this part of the profile series may therefore be looked upon as an expression both of a low degree of saturation and of a very weak acidoid (= relatively strong basoid = high exchange alkalinity).   A combination of these two conditions leads to a highly dilute micellar solution, conducive to a low M^{++}/M^+ ratio of the exchangeable ions.

In the Unden series the Ca/K ratios are much lower in the mineral soil than in the humus layer (except in the lower wet end, which is under the influence of

ground water).   The mineral soil is highly unsaturated, whereas the humus layer contains considerable amounts of exchangeable cations despite the fact that the pH is here the lowest.   All this is in agreement with a Donnan distribution, because the humus acidoids (pH_u about 2) are from 100 to 1,000 times as strong as the mineral acidoids ($pH_u = 4$ to 5).   At the pH prevailing in the podzol, the quotient $\dfrac{y_H + z_H}{x_H}$ will, therefore, be much greater in the humus than in the mineral soil, and since

$$\frac{y_{H^+} + z_{H^+}}{x_{H^+}} = \frac{y_{M^+} + z_{M^+}}{x_{M^+}} \quad \text{and} \quad \left(\frac{y_{M^+} + z_{M^+}}{x_{M^+}}\right)^2 = \frac{y_{M^{++}} z_{M^{++}}}{x_{M^{++}}}, \qquad (G)$$

it follows that the humus must be more thoroughly saturated with bases than the mineral soil and that the Ca/K ratio should be lower in the latter.

The Ca/K ratio in leached soils should, in general, be lower the higher the iso-electric point of the soil.

This relationship in the distribution of the exchangeable cations in the soil is reflected in the composition of the vegetation.   Mattson and Karlsson (15) thus found an average of 89.4 m.e. Ca and 52.4 m.e. K per 100 gm. in 13 species of plants from the wet end of the Dala series of profiles, and 64.4 m.e. Ca and 70.4 m.e. K per 100 gm. in nine species from the dry end.   This yields a Ca/K ratio of 1.71 and 0.91 for the wet and the dry end respectively, despite the fact that the soil is somewhat richer in K in the wet end.

Here is apparently a case of ion antagonism.   In the dry end, where there is a much smaller excess of Ca ions in the soil, the K uptake by the plants is, as a result, both absolutely and relatively greater than in the wet end, despite the somewhat smaller amounts of K in the dry end soil.

Albrecht found the same trend in the composition of crops in relation to the degree of soil development, and reported a K/Ca ratio of 1.2, 1.8, and 4.5 for plants on slightly, moderately, and highly developed soils respectively.

It would thus appear that the consequences of Donnan equilibria in soil formation reach into the realm of plant physiology and, perhaps, into that of plant ecology.

<center>DISCUSSION</center>

In the opinion of some workers the Donnan equilibrium has been too much emphasized in our studies of soil colloidal behavior.   But these experiments seem to us definitely to prove that the soil is a Donnan system.   The "salt-free" layer hypothesis and the hydration theory can each account for the negative adsorption of the free electrolyte ($x > y$), but neither can account for the valence effect in relation to the relative concentration in the inside and outside solution.

Davis (3) asserts that "from the point of view required by the concept of Donnan equilibria, soil systems *per se* are one-phase systems, since there is present on discrete noncolloidal macrophase upon which experiments can be performed.

With the exception of special conditions, Donnan systems in the best sense do not exist in natural soil bodies or in the samples brought into the laboratory."

This raises an interesting question: If a macrosystem such as soil-soil dialyzate or soil sediment-supernatant liquid is a Donnan system, at what moisture content does it cease to be such a system?

It seems to us that the answer to this question is: As long as the soil is moist enough to wet another body and to give off moisture to that body, there is present an extramicellar soil solution, or "noncolloidal phase," which surely does not contain the exchangeable cations and which must therefore exist in a Donnan equilibrium with the micellar solution, which contains these ions. We can even conceive of an experiment being performed on this solution. Suppose, for example, that we place a packet of ashless filter paper (or a porous porcelain plate) tightly in the soil in the field. After some time the paper will have absorbed a certain amount of the soil solution, which can be analyzed. The exchangeable ions present in the micellar solution can then be displaced and their proportion approximately determined.

The point at which a soil no longer wets, at which it no longer feels moist, and at which it assumes the color of a dry soil corresponds probably to that moisture content at which there is no free water, at which the water dipoles all occupy a more or less oriented position around the ions and the colloidal particles. At this point, which corresponds to the "tail end" of the hygroscopic moisture, so to speak, we can no longer conceive of the soil solution as existing in the form of two distinct phases.

But it is not adequate to look upon the soil as a two-phase Donnan system. Our experiments lead to the conception of a polyphase system. The soil is heterogeneous. It contains particles and aggregates, mineral and organic, which have different composition, different isoelectric point, and different charge density. Each microsystem establishes its own equilibrium, which might be very different from that of an adjacent microsystem even though the outside solution be common to both (see table 163 B, where in 0.01 N, the Ca/NH$_4$ ratio is 8.4 and 3.3 for bentonite and laterite respectively).

In the virgin soil a more or less smooth gradient has been established, but when the soil is cultivated, and material from the B horizon is mingled with material from the A horizon (a situation brought about to some degree in all soils by insects, worms, rodents, and by the uprooting of trees, etc.), the soil becomes very heterogeneous and chemically very active (13). Such soils must develop a very irregular microdistribution of monovalent and divalent ions. And this distribution must undergo a constant change with changes in the moisture content.

SUMMARY

An application of the theory of the Donnan equilibrium to soil conditions leads to the following conclusions:

1. Soils having a low cation-exchange capacity, that is, soils which are weak acidoids, such as red earths and laterites, should, other things being equal, contain a higher propor-

tion of exchangeable monovalent cations (Na and K as compared to Ca and Mg) than soils having a high exchange capacity. The former soils possess a lower micellar-ion concentration (a more dilute "inside" solution) and should adsorb the monovalent ions relatively better than the latter.

2. The more unsaturated a soil, the greater should be the proportion of exchangeable monovalent cations. The undissociated acidoid does not participate in the Donnan equilibrium. A highly unsaturated soil has, therefore, a greatly reduced micellar-ion concentration and should adsorb the monovalent cations relatively better than the saturated soils.

3. Among the leached soils the proportion of alkali cations should therefore be greatest in the highly unsaturated soils possessing weak acidoid properties, whereas the proportion of the alkaline-earth cations should be greatest in the slightly leached, saturated soils possessing a high exchange capacity.

These conclusions are supported by the following experimental evidence:

1. Kaolin and a laterite were found to adsorb relatively more NH_4 ions than was adsorbed by bentonite from solutions of NH_4Cl and $CaCl_2$.

2. The bentonite adsorbs relatively more of the monovalent ions, the more unsaturated it becomes.

The conclusions are also supported by analytical data from various sources.

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DYNAMICS OF WIND EROSION: VI. SORTING OF SOIL MATERIAL BY THE WIND[1]

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Soils are composed of individual particles and aggregates varying widely in density, shape, and size. The smaller soil particles are moved by wind of a lower velocity and at a faster rate than the coarser grains of the same shape and specific gravity. Fine dust is carried in suspension with a speed almost equal to that of the wind, whereas coarse erosive grains merely roll and slide along the surface, move but very slowly, and tend to become deposited close to or within the eroding area. Consequently, in attacking the soil the wind tends to separate its component parts, removing the finer and leaving the coarser fractions behind.

In recognizing this sorting action, Udden (7) defines the separations made during the geological process of sand dune formation as follows: (*a*) coarse gravels that the wind cannot move, (*b*) dune sands that are lifted by the wind but can be carried only short distances, (*c*) lee sands, which may be suspended in air for more considerable periods and which are dropped on the lee of the dunes, (*d*) dust, which is carried off into the atmosphere and which may be precipitated with the rain or after the wind has slackened considerably.

A substantial amount of study has been made on the grading of sand by wind (2), but little information has so far been available on the sorting action of wind on arable soils. Daniel (3) found that soil materials carried by wind over coarse- and medium-textured soils and subsequently deposited in drifts contained an average of 37.8 per cent less silt and clay and 29.3 per cent more sand than the adjacent virgin soil. Moss (5) found similar effects on sandy loam soils and virtually no change in texture of clay soils.

The purpose of this paper is to present further information on the essential characteristics and the extent of the sorting action of wind on different types of arable soil.

METHOD OF PROCEDURE

Soil samples were collected from wind-eroded cultivated fields and from newly formed dunes situated next to these fields. The samples of cultivated soil were taken to a depth of 4 inches from fallowed land in the spring following a period of dry weather with high winds. Five individual samples collected from different parts of the field were combined, dried, and throughly mixed. The freshly drifted soils, still unaffected by rain, were obtained from dunes formed along the edges

of the sampled cultivated fields. These samples of drifted soil represent that portion which was moved about by the wind and deposited next to various obstructions, such as fence lines or weeds. The individual samples were taken from different positions on the dunes so as to assure a composite that would represent the average.

As the sorting action of wind depends on the size, specific gravity, and shape of the individual particles and aggregates composing the soil, it was decided to determine these physical characteristics. The direct sieving technique, using a nest of sieves with square apertures, was used to determine the size-frequency distribution of soil clods and granules.

The specific gravity of each fraction separated by sieving was determined by dividing the weight of a definite volume of the fraction by the weight of an equal volume of quartz sand containing the same-sized grains as the soil fraction and multiplying the quotient by 2.65. The quartz sand used was very uniform in composition and had a specific gravity of 2.65.

The effects of variations in shape of the different soil grains could not be determined directly, but the combined effects of the variations in size, shape, and specific gravity were determined from the terminal velocities of fall through still air— the terminal velocity being considered as a constant velocity which an object finally attains when allowed to fall from rest through a fluid. It is attained when the resistance of the fluid against the falling object becomes equal to the downward pull of gravity. The force of gravity depends on the mass of the falling object (which is in turn dependent on its volume and specific gravity), whereas the resisting force of the fluid is dependent on the shape of the object and its velocity of fall. The terminal velocity of fall through air is actually the same as the upward velocity of the wind required to hold the object in midair. A slight increase in this velocity would promptly move the object upward. The terminal velocity of fall can therefore be used to determine the velocity of the wind required to lift and carry soil grains away.

Furthermore, the terminal velocity of fall serves as a convenient method of specifying the equivalent size, shape, and specific gravity of the grains. This may be done by replacing the soil grains by imaginary spheres of some definite material and of such a diameter that they would fall through air with the same terminal velocity as the average grain of the sample. Quartz spheres of 2.65 specific gravity whose terminal velocities of fall through air have been accurately measured (4) were taken as a criterion. These data, along with the data on the terminal rate of fall of soil grains, enabled the measurement of the *equivalent diameter* for the grains. The equivalent diameter was taken as that diameter of a quartz sphere of 2.65 specific gravity whose terminal velocity of fall was equal to the average rate of fall of the soil grains.

The average terminal velocity of fall was determined by experiment. Each soil fraction obtained from sieving was allowed to fall from rest in still air through different vertical distances, and the final constant velocity attained was recorded. A small quantity of soil grains was allowed to fall on a round rotating table from a hopper which was made to open instantly by an electric current. The beginning

of the fall was made to correspond to the time when an arbitary zero radius on the rotating table was directly below the narrow hopper opening.   The exact time of fall was determined from the angle between the zero radius and the radius passing through the average position of the soil grains on the rotating table (which was covered with sticky paper to prevent rebounding of the falling grains).   The distance through which the coarsest fractions used in the experiment had to fall to reach the terminal velocity was about 23 feet, but for the majority of fractions this distance was much less.

The mechanical composition of the soils was determined by the pipette method (6), the organic matter by the Walkley method (8), and the total nitrogen in the usual manner (1, p. 4).

<div align="center">RESULTS</div>

Table 1 shows the proportions of the different sizes of dry soil fractions found in cultivated soils and in newly formed drifts derived from these soils.   The largest particle in the drifts did not exceed 2 mm. in diameter, and most of the soil particles did not exceed 0.83 mm.; yet in the cultivated soils a substantial proportion of much larger fractions and a much greater proportion of the smallest fractions were found.   The predominant diameter of particle in the drifts was between 0.18 and 0.59 mm., depending on soil type, whereas in the cultivated material there was no distinct predominant diameter.   By its action on the soil, the wind effected a general separation of the various constituents, the coarser erosive, semierosive, and nonerosive fractions tending to be left behind and the finer to be deposited in dunes or drifts in the vicinity of the eroded area or, in the case of the finest fractions, to be blown away.

In all cases, the proportion of fractions smaller than 0.05 mm. in diameter was higher in cultivated soils than in the drifts, indicating that a great proportion of these particles tended to sort out from the drifts and to be removed beyond the vicinity of the eroding field.   The wind evidently tended to separate the soil into several distinct grades, as follows: (a) nonerosive clods and rock materials which remained in place; (b) coarse semierosive grains which were moved but slowly with the wind and most of which remained on the surface of the field after the storm; (c) highly erosive grains forming material that was piled into dunes, chiefly along the border of the eroded field; (d) highly erosive grains bordering on dust which tended to separate from the dune materials and became deposited in uniform layers beyond the position of the dunes; and (e) fine dust which, once lifted off the ground, was carried into the atmosphere.   There were evidently no distinct lines of demarkation between these various grades, and each grade merged into the next larger and the next smaller one to a considerable degree. Roughly, the amount of grade b of the above classification was in direct proportion to the amount of soil carried in surface creep, grade c to that carried in saltation, and grades d and e to that in partial and true suspension.

The predominant or the average size of particles forming dunes varied considerably with type of parent material.   The predominant size is more clearly indicated by plotting the percentage weight of each sieve grade against the grain diameter,

TABLE 1

Dry aggregate composition of cultivated and freshly accumulated drift soils

SOIL TYPE	SOIL STATE	GRAINS <1.19 MM. IN DIAMETER*	SIZE DISTRIBUTION OF GRAINS <1.19 MM. IN DIAMETER									
			1.19–0.833 mm.	0.833–0.59 mm.	0.59–0.42 mm.	0.42–0.297 mm.	0.297–0.25 mm.	0.25–0.177 mm.	0.177–0.149 mm.	0.149–0.105 mm.	0.105–0.05 mm.	<0.05 mm.
		per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent
Regina heavy clay........	Cultivated	84.35	6.01	8.33	20.09	19.71	16.37	8.41	7.07	5.12	5.03	3.87
	Drift	99.93	0.46	3.01	14.08	32.38	14.37	16.49	4.98	6.39	4.72	3.05
Sceptre clay............	Cultivated	82.93	14.03	12.36	10.22	9.61	8.78	8.03	6.62	8.03	10.22	12.60
	Drift	99.91	1.39	12.24	18.13	19.54	9.69	12.72	4.87	7.47	8.14	5.72
Fox Valley silty clay loam...	Cultivated	73.89	8.42	11.42	16.91	4.66	4.41	4.21	4.77	13.40	15.12	16.88
	Drift	99.97	0.11	0.49	1.94	9.09	9.41	18.18	8.00	15.24	23.83	13.68
Haverhill clay loam.......	Cultivated	74.14	6.84	9.47	12.26	8.10	5.83	6.37	7.10	11.43	16.46	16.14
	Drift	99.97	0.33	1.66	5.29	11.22	7.75	17.21	8.46	15.72	25.75	6.54
Haverhill loam..........	Cultivated	74.60	5.27	7.64	9.92	6.70	4.27	5.20	4.27	10.50	26.40	20.03
	Drift	99.96	0.11	0.57	1.79	7.90	7.21	17.86	8.61	17.14	29.14	9.63
Hatton fine sandy loam....	Cultivated	88.73	1.73	1.74	3.09	5.34	5.60	12.32	15.82	18.41	20.15	15.80
	Drift	99.98	0.07	0.25	1.00	3.88	4.79	19.26	13.33	21.66	29.69	6.05

* Drift soils contained no grains greater than 2 mm. in diameter.

or better still by plotting the logarithm (to base 10) of the weight of each sieve grade against the logarithm of grain diameter. Bagnold (2) carried out a very comprehensive study of the grain size distribution of dune sand. By plotting the logarithm of the percentage weight of sand per unit of the log-diameter scale against the logarithm of grain diameter, he found that the grades to the right and the left of the predominant or "peak" diameter fell off at a constant rate, the resulting diagram appearing as a cross-section diagram of a common gable roof, minus the peak, which was lopped off and replaced by a tiny arc. The peak diameter can be read off directly below the point at which the two straight arms of the curve (fig. 1) intersect when projected upward.
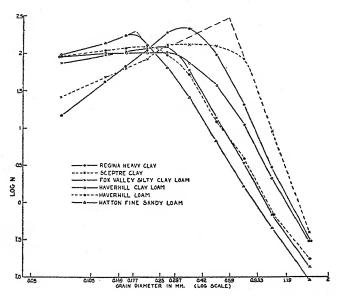
FIG. 1. SIZE DISTRIBUTION OF SOIL GRAINS IN NEWLY FORMED DUNES

Assuming the diameter limits of each grade determined by sieving to be d_1 and d_2, then R, which is the logarithmic interval of grain diameter, is given by ($\log d_1 - \log d_2$) or $\log \frac{d_1}{d_2}$, and the percentage weight P of each grade per unit of log-diameter scale is equal to $\frac{\Delta P}{\Delta R}$ which will be designated as N. By plotting the logarithm of N for the different drift soils of table 1 against the logarithm of grain diameter, diagrams are obtained as shown in figure 1. Except for a few slight kinks, the two arms of each curve are straight lines and agree, at least in essential features, with the grading diagrams found by Bagnold for desert sand. Such marked and consistent grading of drift materials from highly irregular parent materials seems almost incredible in view of the fact that the materials deposited in dunes were in the majority of cases a result of a single dust storm! In his wind tunnel grading experiments, Bagnold found a strong tendency of grading

TABLE 2

Specific gravity and equivalent diameter of different sizes of grains in drifted soils

ACTUAL GRAIN DIAMETER	REGINA HEAVY CLAY		SCEPTRE CLAY		FOX VALLEY SILTY CLAY LOAM		HAVERHILL CLAY LOAM		HAVERHILL LOAM		HATTON FINE SANDY LOAM	
	Specific gravity	Equivalent diameter	Specific gravity	Equivalent diameter	Specfic gravity	Equivalent diameter	Specific gravity	Equivalent diameter	Specific gravity	Equivalent diameter	Specific gravity	Equivalent diameter
mm.		*mm.*		*mm.*		*mm.*		*mm.*		*mm.*		*mm.*
0.05 –0.10	1.88	0.043	1.89	0.044	1.72	0.039	2.04	0.041	2.18	0.042	2.43	0.065
0.10 –0.149	1.82	0.068	1.86	0.069	1.68	0.063	1.98	0.073	2.05	0.081	2.39	0.091
0.149–0.177	1.87	0.092	1.80	0.090	1.65	0.080	1.76	0.088	2.05	0.101	2.36	0.116
0.177–0.25	1.85	0.118	1.72	0.112	1.70	0.111	1.70	0.109	1.98	0.126	2.33	0.150
0.25 –0.298	1.86	0.158	1.75	0.145	1.64	0.137	1.64	0.133	1.80	0.151	2.19	0.183
0.298–0.42	1.86	0.208	1.70	0.189	1.67	0.183	1.60	0.172	1.74	0.178	2.22	0.240
0.42 –0.59	1.83	0.281	1.72	0.264	1.58	0.245	1.48	0.220	1.60	0.247	1.96	0.299
0.59 –0.83	1.70	0.365	1.72	0.364	1.47	0.316	1.40	0.301	1.47	0.321	1.74	0.366
0.83 –1.19	1.60	0.494	1.60	0.498	1.43	0.406	1.38	0.422	1.50	0.456	1.40	0.436
1.19 –2.0	1.48	0.708	1.53	0.734	1.39	0.561	1.39	0.680	1.36	0.630	1.31	0.596

of irregular sands to this characteristic pattern, although no complete establishment of a logarithmic relation between N and grain diameter was obtained by single exposure in every case, as that occurring in drift soils herewith reported. It must be remembered, however, that while the tunnel was only 30 feet long, the eroding areas adjacent to which these drift materials were collected were from $\frac{1}{4}$ to $\frac{1}{2}$ mile in length—a distance apparently sufficient for effecting an ultimate selection of the blown material.

The values of log N in figure 1 were plotted against the logarithm of the actual diameter of the grains which, as shown in table 2, varied considerably in specific gravity, both as to type of the parent material and as to size of the individual particles or aggregates of which the drift materials were composed. In all
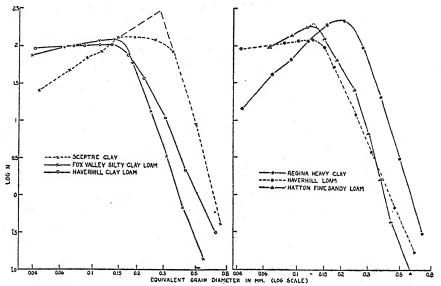
FIG. 2. SIZE DISTRIBUTION OF SOIL GRAINS IN NEWLY FORMED DUNES

cases the coarsest grades were of the lowest specific gravity, and the finest grades were of the highest. The ratio of the lowest to the highest specific gravity was in some soils approximately 1 to 1.75. Such large variations were considered too great to be ignored. Hence, equivalent diameters were determined, and the logarithms of these were plotted against the log N values for the different grades (fig. 2). As before, the diagrams indicated the same logarithmic law of distribution, but the position of the individual curves was narrowed down considerably. Whereas the values of the actual peak diameter (fig. 1) ranged from 0.18 to 0.59 mm., the values of the equivalent peak diameter (fig. 2) varied only from 0.13 to 0.28 mm. for the same materials. The high peak diameter for the clay drifts of figure 1 was probably due to the exceptionally high degree of porosity of the parent soil material. The degree of porosity, however, cannot be accepted as the only factor that might affect the peak diameter of the grains, for if such were the

TABLE 3

Organic matter content, nitrogen, and mechanical composition of cultivated and drifted soils

SOIL TYPE	SOIL STATE	ORGANIC MATTER	NITROGEN	MECHANICAL COMPOSITION OF DISPERSED SOIL MATERIAL							
				2-1 mm.	1-0.5 mm.	0.5-0.25 mm.	0.25-0.10 mm.	0.10-0.05 mm.	0.05-0.005 mm.	0.005-0.002 mm.	<0.002 mm.
		per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent
Regina heavy clay........	Cultivated	4.50	0.280	0	0.2	0.3	1.2	7.6	29.9	15.0	45.9
	Drifted	4.90	0.296	0	0.1	0.3	1.6	7.3	31.9	15.1	43.9
Sceptre clay........	Cultivated	4.96	0.272	0.2	0.6	1.5	6.7	8.6	33.2	7.6	39.9
	Drifted	4.92	0.247	0	0.6	1.5	5.7	8.9	39.7	7.3	37.0
Fox Valley silty clay loam.......	Cultivated	3.32	0.223	0.1	0.1	0.5	1.8	16.6	58.0	8.7	13.5
	Drifted	4.21	0.231	0	0.1	0.5	3.8	18.0	52.4	11.7	15.3
Haverhill clay loam.......	Cultivated	4.08	0.230	4.0	4.2	6.0	12.7	15.7	37.5	11.2	12.4
	Drifted	3.76	0.256	0	0.4	2.0	23.9	24.8	28.4	8.9	10.6
Haverhill loam.......	Cultivated	4.04	0.212	1.8	1.3	2.4	8.8	22.2	43.2	6.3	13.0
	Drifted	3.42	0.153	0	0.1	1.6	29.5	24.4	26.0	3.2	11.8
Haverhill light loam.......	Cultivated	3.14	0.189	0.4	0.8	5.6	18.9	23.2	28.8	4.8	14.6
	Drifted	3.82	0.171	0	0	4.3	29.7	26.7	21.6	5.5	10.0
Hatton fine sandy loam.......	Cultivated	3.35	0.213	2.5	0.5	2.6	26.4	27.4	29.0	3.4	8.8
	Drifted	1.80	0.096	0	1.0	4.4	57.4	15.7	12.0	3.8	5.2

case the dune material drifted off Fox Valley silty clay loam should show the highest peak diameter, when actually it showed nearly the least. The drifted soils were all collected in the same vicinity and after the same windstorm so as to make reasonably certain that nearly the same wind force acted on all the drifted soils. It is evident that the nature of the parent material greatly influenced the physical composition of the drifted soil.

On the average, the drifted soil materials were found to be more sandy than the corresponding cultivated soils. The greatest tendency toward an increased sandy condition of the drifts was found in Hatton fine sandy loam (table 3) and the least, or none at all, in clay soils. The results confirm those of Moss (5) on other soil types. No mechanical fractions greater than 1 mm. and only small quantities of sand coarser than 0.5 mm. in diameter were found in the drift materials, indicating that erosive quartz grains seldom exceed 0.5 mm. in diameter. In fact, the average diameter of erosive quartz grains is much smaller than this, as indicated by the fact that not more than 6 per cent of the sand grains in the drifts failed to exceed 0.25 mm. in diameter.

The amount of organic matter and nitrogen in all soils, except Hatton fine sandy loam, was found to be about the same in drifted as in the corresponding cultivated soils (table 3). In Hatton fine sandy loam both organic matter and nitrogen were considerably lower in the drifted than in the residual soil, indicating that much of these constituents has been blown away from the drifting area. The results by no means suggest that there was no appreciable loss of organic matter and nitrogen from the remaining wind-swept cultivated soils shown in table 3, but merely indicate no appreciable difference between the transported and the residual soil material. In order to determine the actual losses, analyses of the wind-eroded cultivated soils and of the corresponding noneroded virgin soils must be made.

SUMMARY

It was shown that the wind tends to remove large quantities of fine dust from cultivated fields, but the less mobile grains, none of which exceed 2 mm. in diameter, pile up into dunes or remain in a more or less uniform layer in the vicinity of the eroded area.

The size distribution of particles contained in the dunes was found to conform to a definite logarithmic relationship originally discovered by Bagnold in desert sand.

For soils deposited in dunes under apparently the same wind force, the actual peak diameter varied from 0.18 mm., for Hatton fine sandy loam, to 0.59 mm., for Sceptre clay. The equivalent peak diameter varied only from 0.13 to 0.28 mm., for the same soils.

On the average, the drift soils were considerably more sandy than the corresponding cultivated soils, indicating that much of the fine material in the form of silt and clay was blown away. The greatest sorting of the mechanical fractions was on fine sandy loam, the least, if any, on fine clay.

With the exception of Hatton fine sandy loam, the amount of organic matter

and nitrogen was found to be about the same in the drifted as in the corresponding residual soil material.

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FLUORINE IN SOILS

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Recently much interest has been shown in fluorine in its relation to biochemisty both as a toxic element and as an element thought necessary for the development of healthy teeth in humans.

Many excellent recent reviews of the literature on the biological aspects of fluorine have appeared. Reference is made to the reviews of Roholm (21), Machle, Scott, and Treon (13), Pierce (20), Greenwood (8), Murray (18), and Mitchell and Edman (17).

Very few data are available on the fluorine content of soils, and this contribution is offered to supply this want. Steinkoenig (23) in 1919 found from none to 1,500 p.p.m. of fluorine in fifteen samples from nine locations in eastern United States. The average of the fifteen determinations is 240 p.p.m. The analytical method he employed is reliable but not sensitive. McIntire *et. al.,* (15) report 80, 93, 103, 109, 125, and 338 p.p.m. fluorine in surface soils, locations not given but presumably from Tennessee.

SOURCES OF FLUORINE IN SOIL

According to Clarke and Washington (1) fluorine averages 290 p.p.m. in the 10-mile-deep crust of igneous and sedimentary rocks. Fluorine is an essential element in the following minerals: fluorite, apatite, cryolite, topaz, phlogophite, lepidolite, zinnwaldite, and other less important minerals. Such very common soil minerals as biotite and muscovite may contain as much as 4 and 2 per cent fluorine respectively, and hornblende and tourmaline contain smaller quantities. The figures given for biotite and muscovite are maximum as given by Dana (4), and not all muscovite and biotite will contain as much, though these minerals always seem to contain some fluorine, generally more than traces. Muscovite, biotite, and hornblende are exceedingly common soil minerals and would seem to be the main source of fluorine in soils. Steinkoening reports the original source of fluorine in the soil as the micas, apatite, and tourmaline in the parent materials.

McIntire and Hatcher (14) consider that phosphorus is "fixed" in the form of apatite in soils containing an excess of lime. Nagelsmith and Nixon (19) found that superphosphate, added continuously since 1852 to a heavily limed plot at Rothamstead, England, had been fixed as apatite. McIntire *et al.* (15) have

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estimated that the annual rainfall brings down 0.15 pounds per acre of fluorine at a certain place in Tennessee.   Many soft coals contain as much as 100 p.p.m. F.[3]

Fluorine, unlike chlorine, is not concentrated in sea water but appears to be strongly absorbed by the soil (6).[4]   Thompson and Taylor (24) give the fluorine content of sea water as 1 to 1.4 p.p.m.

Volcanic gases contain considerable fluorine.   In fact, the first record of fluorine toxicity is from Iceland where many sheep died from eating pasturage made toxic by the fluorine thrown out by the eruption of a volcano.   Some soils undoubtedly have been enriched in fluorine from volcanic sources.   Finally, there are three sources of artificial fluorine enrichments: first, the fluorine in superphosphate, which contributes considerably to the fluorine in cultivated soils; second, local enrichments due to the widespread use of fluorine in various manufacturing processes; and third, the growing use of fluorides as insecticides.

In 1944 the United States and territories used 8,640,000 tons of mixed fertilizer averaging about 0.70 per cent F; 1,640,000 tons of superphosphate averaging about 1.50 per cent F; 196,300 tons rock phosphate averaging 3.8 per cent F; and 81,000 tons double superphosphate averaging 1.56 per cent F.   This makes, in round numbers, 93,800 tons fluorine added annually to rather restricted areas under cultivation.

Considerable quantities of fluorides are used or evolved in the manufacture of aluminum, phosphatic fertilizers, bricks, enamelled ware, high octane gasoline, glass and in other industries.   Soil enrichments from these sources are only local. Because fluorides are expensive, useful as insecticides, and toxic if let loose in the atmosphere, every effort is made to recover the fluorine in industrial operations.

The fluorine added to the soil by the application of insecticides is presumably small, local, and therefore of little general consequence.

FLUORINE CONTENTS OF SOILS

The total fluorine content of a number of representative soils is given in table 1. The soils analyzed were selected to include a variety in series, textures, parent materials, and geographic distribution.   McIntire's method (16) has been used for many of the determinations.[5]   The analytical figures in parts per million are reproducible to two and occasionally three significant figures if the first digit is small.   The analytical results are given to three significant figures throughout the table with the realization that the third digit is an *approximation*.

In the clay loam from Caribou County, Idaho, and in the lower horizons of Maury silt loam it is quite evident that the greater part of the fluorine is in the form of phosphate rock.   The P_2O_5 content of the fourth horizon of the Maury is 8.3 per cent.   In these soils, there is a fairly good correlation between the fluorine and phosphorus contents, which are very high.   Aside from these two series, however, there is no correlation between the fluorine values given here and the phosphorus values available in other publications and data in this Division.

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[3] F. C. Frary, privately communicated.

[4] Also L. A. Dean, privately communicated.

[5] About half of the analyses were made by this method in this Bureau by G. J. Hough (deceased) under the direction of H. G. Byers (retired).

TABLE 1
Total fluorine in soils

SOIL TYPE	LOCATION	LABORATORY NUMBER	DEPTH	FLUORINE
			inches	*p.p.m.*
Arredonda fine sand	Gainesville, Fla.	C-6331	0–36	20
Barnes loam	La Bolt, S. D.	C-2929	0– 9	220
		C-2930	9–17	232
		C-2931	17–33	357
		C-2932	33–60	390
Brassua sandy loam	North Grafton, N. H.	C-1438	0– 3	22
		C-1439	3– 4	70
		C-1440	4– 9	62
		C-1441	9–19	97
		C-1442	19+	92
Bridgeport loam	Sheridan, Wyo.	D-4682	0– 3	270
		D-4683	3– 7	335
		D-4684	7–15	388
		D-4685	15–20	440
		D-4686	20–27	487
		D-4687	27–34	461
Carrington loam	Winthrop, Iowa	C-2916	0– 3	120
		C-2917	3–13	127
		C-2918	13–22	130
		C-2919	22–43	190
		C-2920	43–70	150
		C-2921	70–84	210
Chester silt loam	Rockville, Md.	C-3315	0– 1	170
		C-3316	1– 9	175
		C-3317	9–20	250
		C-3318	20–26	307
		C-3319	38–41	380
Chester silt loam	Falls Church, Va.	C-5227	0– 8	137
		C-5228	12–24	172
Unidentified clay loam	Caribou Co., Idaho	B-26607	0–12	1640
		B-26608	12–24	3870
Colby silty clay loam	Hays, Kans.	6842	0–10	N.D.*
		6843	10–20	403
		6844	20–33	495
		6845	33–47	522
		6846	47–60	525
		6847	60–72	491

TABLE 1—*Continued*

SOIL TYPE	LOCATION	LABORATORY NUMBER	DEPTH	FLUORINE
			inches	*p.p.m.*
Fayette silt loam	LaCross, Wis.	10362	0– 8	187
		10363	8–20	215
		10364	20–32	246
		10365	32–44	280
		10366	44–66	232
Frederick silt loam	Fairfield, Va.	C-807	0– 2	207
		C-808	2–11	145
		C-809	11–16	287
		C-810	16–36	1032
		C-811	36–56	1305
Greenville Sandy loam	Pretoria, Ga.	C-1063	½– 2	28
		C-1064	2– 7	52
		C-1065	7– 15	38
		C-1066	15– 24	44
		C-1067	24– 42	93
		C-1068	42– 72	113
		C-1069	72–108	184
Hagerstown silt loam	State College, Pa.	C-798	0– 2	260
		C-799	2– 8	310
		C-801	14–35	720
		C-802	35–46	902
Hagerstown silt loam	Hagerstown, Md.	C-803	0– 3	332
		C-804	3–12	352
		C-805	12–33	1832
		C-806	33–48	1910
Holdredge silt loam	Custer County, Neb.	C-7710	0– 2	240
		C-7711	2–12	285
		C-7712	12–24	432
		C-7713	24–36	490
		C-7714	36–60	432
		C-7715	60–72	457
Houston black clay	Temple, Tex.	6096	0– 3	372
		6097	14–20	416
		6098	24–36	425
		6099	36–50	364
Kalkaska loamy sand	Alger Co., Mich.	C-7725	0– 2	20
		C-7726	2– 6	tr.
		C-7727	6–24	12
		C-7728	24–48	15

TABLE 1—*Continued*

SOIL TYPE	LOCATION	LABORATORY NUMBER	DEPTH	FLUORINE
			inches	*p.p.m.*
Kirvin fine sandy loam	Tyler, Tex.	6678	0–12	48
		6679	12–24	334
		6680	24–51	299
		6681	51–63	133
		6682	63–75	58
Madison sandy loam	Gainesville, Ga.	C-4649	0– 6	234
		C-4650	6–18	269
		C-4651	18–30	235
		C-4652	30–36	300
		C-4653	36–40	334
Marshall silt loam	Clarinda, Iowa	8736	0–13	376
		8737	13–24	411
		8738	24–45	394
		8739	45–71	296
Maury silt loam	Ashwood, Tenn.	C-128	0– 2	500
		C-129	2–12	290
		C-130	12–25	850
		C-131	25–40	7070
		C-132	40–60	4300
		C-133	60–90	4080
Miami silt loam	Wayne Co., Ind.	4060	0– 2	95
		4061	2– 5	130
		4062	5–11	135
		4063	11–15	187
		4064	15–30	400
		4065	30–36	452
Muskingum silt loam	Zanesville, Ohio	B-407	0– 7	316
		B-408	8–13	390
		B-409	14–24	344
		B-410	25–46	326
		B-411	47–72	365
Norfolk sandy loam	Bests, Wayne Co., N. C.	294	0–12	42
		295	12–34	70
		296	36–80	95
Oahu clay	Oahu, Hawaii	C-1649	0–10	120
		C-1650	10–25	87
		C-1651	25–40	55

TABLE 1—*Continued*

SOIL TYPE	LOCATION	LABORATORY NUMBER	DEPTH	FLUORINE
			inches	*p.p.m.*
Palouse silt loam	Pullman, Wash.	8069	0–20	369
		8070	20–33	364
		8071	33–62	360
		8072	62–75	389
		8073	75–84	358
Shelby silt loam	Bethany, Missouri	6797	0– 7	276
		6798	8–12	414
		6799	12–20	487
		6800	20–24	468
		6801	24–48	438
		6802	48–60	442
		6802a	48–	306
		6802b	60–84	420
Redding clay loam	San Diego Co., Calif.	4537	0– 7	85
		4538	7–14	106
		4539	14–24	130
		4540	24–33	105
		4541	33–41	146
		4542	41–51	154
Sharkey clay	Houma, La.	C-2106	0– 6	590
		C-2107	10–24	525
		C-2108	48–80	620
Vernon fine sandy loam	Guthrie, Okla.	6718	0– 3	40
		6719	3–10	85
		6720	10–27	183
		6721	27–58	293

* Not determined.

Perhaps the most characteristic feature of fluorine distribution in the soil is the general tendency of fluorine to increase with depth in the profile. If only the surface and subsurface soils were involved it might be thought that in common with some other minor elements, the fluorine was mainly present in the fine clay or colloid particles. In many cases, however, the fluorine increases in the C horizon, and there is not necessarily a maximum in the B horizon where clay usually accumulates.

A tentative explanation can be offered for the observed increase in fluorine content with depth of soil. Denison *et al.* (5) observed that comparable micaceous fragments separated from the soil were higher in potassium in the lower horizons of a profile than in the horizons near the surface. In fact, in some cases these micaceous particles near the surface approached kaolin in composition, whereas in the lower part of the profile the composition of unaltered muscovite was shown. There were many gradations between these limits.

Rather convincing evidence of an important source of fluorine in the soils is afforded by the analysis of some micaceous clays purified and submitted by Dr. C. S. Ross of the U. S. Geological Survey to this Division for analysis. The fluorine contents of these clays are given in table 2.

Wislicenus, quoted by Roholm (21), examined the clay being used in a brick kiln that was damaging a forest. He found 1,600 p.p.m. fluorine in this clay.

These examples serve to show that micaceous minerals, though finely divided, may contain a relatively large quantity of fluorine.

The fluorine in the soil analyzed ranges from a trace in the Kalkaska loamy sand to 7,070 p.p.m. in the fourth horizon of Maury silt loam. In general, the sandy soils are low and the heavier textured soils are high in fluorine. The average for the surface layers to approximately plow depth is about 292 p.p.m. This is surprisingly close to the average in the 10-mile crust given by Clarke and Washington (1). It has been pointed out that muscovite, biotite, and other micas are the probable source of much of the fluorine in soils. It is likely that the fluorine in the micas of the surface soils would be leached out along with the potassium. It has been shown by a number of investigations that plants nor-

TABLE 2
Fluorine content of certain micaceous clays

MINERAL	LOCATION	FLUORINE
		p.p.m.
Hydrous mica	Platteville, Wis.	5800
Muscovite	Staley, N. C.	400
Ordovician bentonite	Chattoga Co., Ga.	4500
Ordovician bentonite	Sevier Dam, Tenn.	7400
Serecite	Guanajuato, Mex.	1800
Serecite	Staley, N. C.	300

mally contain very little fluorine; therefore, little of this element would be brought up from lower depths by plant roots and deposited on the surface, the way calcium, for instance, is deposited on the surface by plant remains.

FLUORINE IN SOIL AND CORRESPONDING COLLOID

A few analyses of soils and their extracted colloid are available. They are given in table 3.

The data in table 3 show a considerable concentration of fluorine in the colloidal matter. In Wooster silt loam with 14.6 per cent colloid and 184 p.p.m. F, it is calculated that the 85.4 per cent of the noncolloidal matter contributes but 63 p.p.m. fluorine to the whole soil, whereas 121 p.p.m. is contributed by the 14.6 per cent colloid. With the exception of Sable silty clay loam, part of the fluorine present in all the soils has been contributed by added superphosphate.

ACCUMULATION OF FLUORINE IN SOIL DUE TO SUPERPHOSPHATE FERTILIZATION

The addition of 1,000 pounds superphosphate to an acre of ground would result in increasing by 7.5 p.p.m. the fluorine content of the soil to plow depth. This

TABLE 3

Fluorine content of soil and extracted colloid

SOIL	LOCATION	SOIL NO.	COLLOID	F IN SOIL	F IN COLLOID
			per cent	*p.p.m.*	*p.p.m.*
Caribou loam*..............	Presque Isle, Maine	E-1548	18.2	390	850
Decatur clay loam*.........	Near Decatur, Ala.	E-1563	40.9	178	268
Herrick silt loam*...........	Carlinsville, Ill.	E-1646	17.9	311	664
Sable silty clay loam†........	Aledo, Ill.	E-1648	25.9	220	530
Wooster silt loam*..........	Wooster, Ohio	E-1649	14.6	184	831
Hagerstown silt loam*........	State College, Pa.	E-1670	22.9	316	578

* Superphosphate added.
† No superphosphate added.

TABLE 4

Fluorine content of soils heavily fertilized for long periods, compared to similar, nearby unfertililized soils

SOIL	LOCATION	SOIL NO.	TREATMENT	DEPTH	F
				inches	*p.p.m.*
Collington sandy loam	Near Auburn, N. J.	E-1151	Fertilized 40 years	0– 6	90
		E-1152	Fertilized 40 years	8–12	92
		E-1153	No fertilizer	0– 4	66
		E-1154	No fertilizer	6–14	70
Hagerstown loam	State College, Pa.	E-2173	No F added	Surface soil	311
		E-2177	No F added	Surface soil	292
		E 2178	No F added	Surface soil	263
		E-2174	No F added	Surface soil	276
		E-2175	No F added	Surface soil	311
		E-2176	44 ppm F added	Surface soil	357
		E-2169	88 ppm F added	Surface soil	405
		E-2170	21 ppm F added	Surface soil	364
		E-2171	42 ppm F added	Surface soil	395
		E-2172	84 ppm F added	Surface soil	289
Sassafras gravelly sandy loam	Swedesboro, N. J.	E-1146	Fertilized 23+ years	0– 8	70
		E-1147	Fertilized 23+ years	8–12	64
		E-1148	No fertilizer	0– 5	44
		E-1149	No fertilizer	7–14	46
Sassafras loam	Deerfield, N. J.	E-1160	Fertilized 30 years	0– 6	188
		E-1161	Fertilized 30 years	10–14	138
		E-1162	No fertilizer	1– 6	114
		E-1163	No fertilizer	12–18	120
		E-1164	No fertilizer	22–26	130
Weathersfield loam	No. Arlington, N. J.	E-1136	Fertilized 40 years	0– 8	294
		E-1137	Fertilized 40 years	12–16	194
		E-1138	No fertilizer	1– 5	150
		E-1139	No fertilizer	7–12	172
		E-1140	No fertilizer	12–16	172

is a heavy application, but such applications are used in some intensely cultivated areas. It is possible to form a rough estimate of fluorine accumulations in the soil due to superphosphate applications by comparing the fluorine content of the

fertilized soil with similar soils that have not been fertilized. The fluorine content of soils heavily fertilized for a considerable time as compared to similar unfertilized soils[6] is given in table 4.

The data show a consistent picture with respect to the New Jersey samples. The fertilized soils are all higher in fluorine than the corresponding nonfertilized soils. This difference is greatest with respect to the heavier textured soils. The coarser textured soils show less difference. The fluorine in the unfertilized soils increases with depth, whereas the surface layers of the fertilized soils are higher in fluorine than the subsurface layers, with one exception—that of Collington sandy loam. Here the surface layers are shallow, and the texture is so coarse that it could hardly be expected to retain much fine material. If the quantity of fertilizers used and the probable fluorine content are assumed, rough calculation can be made of the percentage of fluorine retained by the different soils. For Weathersfield loam, fertilization of which increases the fluorine content of the surface by 144 p.p.m. and that of the subsurface by 22 p.p.m., the percentage of fluorine retained is about 60. Next comes Sassafras loam: surface increase, 74 p.p.m.; subsurface increase, 18 p.p.m.; 30 per cent retention. Sassafras gravel sandy loam follows: surface increase, 26 p.p.m.; subsurface increase, 18 p.p.m.; 20 per cent retention. Collington sandy loam has the lowest fluorine retention: surface increase, 24 p.p.m.; subsurface increase, 22 p.p.m.; 7 per cent retention.

There is evidently very little uniformity in the fluorine content of the Hagerstown loam plots with respect to fluorine. Jeffries (10) has reported fluorite in the heavy mineral fractions of this soil, and one would expect the distribution of fluorite to be very uneven in a limestone residual soil. The no-fluorine plots vary from 263 to 311 p.p.m. F, with an average of 293. The average of the plots to which fluorine has been added is 362. The average increase, 69 p.p.m., is not unreasonable though slightly more than the average added.

Fluorine extraction from soil by plants

The paucity of data on fluorine uptake by plants is principally due to the difficulty of analyzing plants for their very small fluorine content.

Sprengel (22) in 1828 asserted that fluorine must occur in plants because it was found in the teeth and bones of animals. For a long time there were no quantitative data on the fluorine content of plants. In 1910 Gautier and Clausmann (7) determined the fluorine in 64 samples of vegetation by an ingenious but complicated method, which now seems to us to give large positive errors in many instances. It is possible, however, that the plants they analyzed may have been contaminated by fluorine in the atmosphere released by burning soft coal or by some other industrial process. Gautier and Clausmann reported the high results of 139, 134, and 85 p.p.m. fluorine in sorrel, beet leaves, and ferns, respectively, on a dry-weight basis. They obtained reasonably low results for some samples such as string beans, 2.1 p.p.m.; carrots, 3.6 p.p.m.; potato tubers, 3.0 p.p.m.

[6] The soils from New Jersey area were collected by E. J. Rubins of this Bureau, and those from State College, Pennsylvania, were furnished by J. W. White of that institution.

But, in the main, their results are much higher than have been obtained for uncontaminated plants.

In 1933, Willard and Winter (25) developed an accurate and sensitive colorimetric method suitable for small quantities of fluorine. This method has been modified by Dahle, Bonner, Wichmann (3) and others for use in plant and food analysis. Recently a number of analyses of plant materials have appeared

TABLE 5
Fluorine content of plant materials grown on Chester loam
Dry-weight basis

PLANTS	FLUORINE
	p.p.m.
Alfalfa, in bloom	2.1
Beans, lima, seeds	2.2
Beans, string, edible pods	4.8
Beans, string, edible pods, fall, 1943	3.2
Beets, roots	4.3
Beet roots, sugar beet type 1943	3.3
Beet tops	3.4
Cabbage, edible head	3.4
Carrot, roots	8.4
Celery, edible stalks	8.5
Corn, leaves only	7.9
Lespedeza sericea, plant above ground	2.2
Lettuce, loose head	11.3
Oxalis, plant above ground	5.1
Parsley, tops	11.3
Parsnip, roots	5.5
Pea vines in bloom	7.3
Peanuts, kernels	1.5
Peanuts, tops	1.7
Poke, young shoots	42.3
Potatoes, Irish, tubers	1.4
Rutabagas, tops	7.0
Rutabagas, roots	2.9
Spinach	28.3
Tomato, fruit	None detected
Tomato, shoots and leaves not including main stem	5.4
Turnip, roots	2.6
Turnip, tops	1.7

(2, 12, 13, 14). These analyses show, in general, that plants are considerably below 10 p.p.m. (dry-weight basis) with the exception of tea, which is definitely a fluorine accumulator. Commercial dried tea leaves as taken from Clifford's data averaged 97 p.p.m. fluorine and may reach as high as 400 p.p.m. The plant gifblaar (11) also contains considerable fluorine and apparently owes its poisonous properties to fluorine in the form of fluoracetic acid.

McIntire *et al.* (15) have reported on the fluorine content of Sudan grass, crimson

clover, and radishes raised on soils of known fluorine content and on the same soils to which as much as 2,300 p.p.m. fluorine had been added. The fluorine content of Sudan grass ranged from 1 to 5 p.p.m.; radish tops from 3 to 25 p.p.m.; red clover 5 to 20 p.p.m.; and sweet clover, 5 to 9 p.p.m. These investigators conclude from the results obtained in the cultures of sweet clover, red clover, and Sudan grass that "no enhancement in the fluorine content of forage crops is to be expected from the conventional use of fluoride-bearing fertilizers and liming materials." Earlier work by Hart, Phillips, and Bohstedt (9) confirms this important observation that the fluorine of fertilizers does not significantly increase the fluorine content of plants.

A number of plants growing on Chester loam from Falls Church, Virginia, have been analyzed for fluorine. The fluorine content of this soil was 137 p.p.m. for the surface and 172 p.p.m. for the subsurface. The pH of the surface was 6.7 and that of the subsurface 5.5. This soil had been liberally supplied with superphosphate for about 15 years and was sproutland about 25 years before being cleared and cultivated. The samples were collected in 1938. The small area on which the samples were grown is surrounded by trees and seems free from the possibility of atmospheric contamination. There were no known industrial sources of contamination nearer than about 10 miles, and these were limited to relatively small superphosphate and brick manufacture near Alexandria and the relatively small quantity of soft coal used in Washington. Both of these are in a direction away from the prevailing wind. No fluoride-containing insecticides were used in or near the garden. The results of analyses are given in table 5.

The data in table 5 show a tendency of seeds and fruit to be lower in fluorine than the leafy and root parts of the plant. Few items exceeded 10 p.p.m. fluorine, and many are less than half this quantity. Poke and spinach have a high fluorine content. It would seem that these plants are, in a measure, fluorine accumulators. It is possible, however, that there has been some fluorine contamination in drying and storage for 7 years in the laboratory. Evidence from more samples is needed.

It is possible, also, that there are some positive errors due to soil contamination of the other plants, especially of the roots. Considerable care was taken in washing the roots and, since the soil is not high in fluorine, the degree of such contamination is probably small. An error in the other direction has been pointed out by F. C. Frary.[7] He asserts that as much as half the fluorine in leaves may be lost on drying if a large part of the fluorine is from atmospheric absorption. He believes, however, that loss on drying of fluorine that has been absorbed from the soil is not important. All our samples were air-dried in the laboratory.

SUMMARY

The fluorine content of 30 profiles, 137 samples in all, of representative soils of varied texture, parent material, and geographic distribution are given. This

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[7] Private communication.

fluorine content varies from a trace to 7,070 p.p.m. in an unusual Tennessee soil containing phosphate rock. The average for surface soils is 292 p.p.m. In general, the fluorine content increases with the depth of the soil. Fluorine is considerably concentrated in the colloidal matter.

Much of the fluorine in soils highest in fluorine is in the form of apatite. Evidence, however, is presented to show that, in general, the main source of fluorine in the ordinary soil is the micaceous clays. In general, there is no correlation between the phosphorus and fluorine contents of soil where the fluorine present is not mainly in the form of apatite.

It is shown that six samples of micaceous clays, which probably occur in soil, have fluorine contents ranging from 300 to 7,400 p.p.m. averaging 3,730 p.p.m. One Ordovician bentonite contains the maximum quantity of fluorine.

Much of the fluorine added to the soil in the form of superphosphate is retained by the heavier textured soils. Coarse, sandy soils retain less of the added fluorine. Added fluorine in the form of superphosphate does not appear to increase significantly the fluorine content of plants.

The fluorine contents of 28 samples of vegetation grown on a soil of known fluorine content are given. It is pointed out that there is very little chance of fluorine contamination in these samples.

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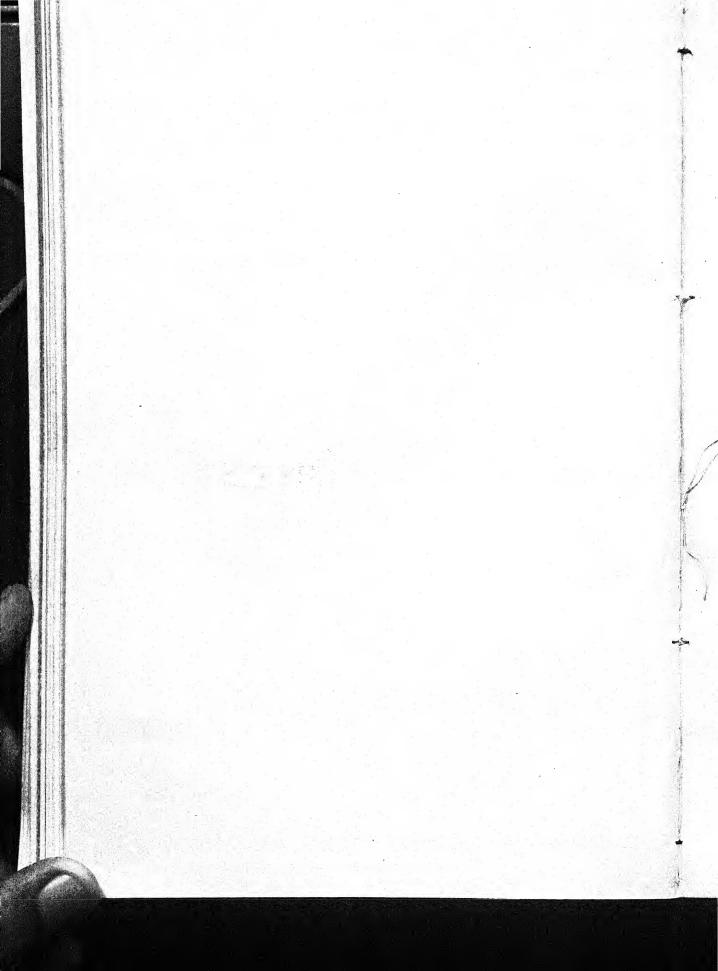
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DISPLACEMENT OF SOIL-AIR BY CO$_2$ FOR PERMEABILITY TESTS

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Recent papers (2, 4) showed that air is entrapped in soils when they are wetted for permeability tests. This air is gradually dissolved by the water passing through the soil, which results in a concomitant increase in permeability. Long periods of time sometimes elapse before all of the air is dissolved and the maximum permeability rate obtained. It was further shown that when the air is evacuated from the soil before wetting, the permeability is at a maximum at the beginning of the test; however, removal of air by evacuation is tedious, and it is difficult to avoid undesirable compaction of the soil column during the process.

In recent tests the air in the soil pores was displaced with CO$_2$ by passing the dry gas through the soil before wetting. Since CO$_2$ is very soluble, it is quickly dissolved by the percolating water, and the maximum permeability is reached within a few minutes. This technique appears to have practical value in connection with experiments in which it is desirable to determine soil permeability during complete saturation. This paper presents permeability data for several soils from which the air has been displaced with CO$_2$, and compares these results with those obtained using an ordinary wetting procedure.

EQUIPMENT AND TECHNIQUE

Permeability determinations were made on 20 soils by a technique described elsewhere (2), except that only 100 gm. of air-dried soil (2 mm.) was used instead of 200 gm. The soil samples were poured into the glass percolation tubes (approximately 35 mm. diameter) through a 14-mm. inside-diameter glass tremie tube with a funnel on top. The capacity of this tube and funnel was sufficient to hold the 100-gm. sample. The percolation tubes were filled by gradually raising and rotation the tremie tube while distributing the soil in a circular path inside the percolation tube. By this method, which is similar to that used by Wadsworth and Smith (5) and by Moore (3), it is possible to place the soil with a minimum of segregation of coarse and fine particles. The soil was settled by placing the percolation tube in a suitable guide and dropping it on its point on a soft wood block ten times through a distance of 2.5 cm.

The CO$_2$ gas was passed through the air-dry soils from the surface downward

at a rate of about 150 ml. per minute. In a preliminary test, the volume of CO_2 passed through the 100-gm. samples of soil was varied from 200 ml. to 2,000 ml. without apparent differences in results. Thereafter, approximately 500 ml. was used in all cases. The gas was applied by means of a delivery tube passing through a stopper fitted to the top of the percolation tube and extending to within half an inch of the soil surface. Most of the air in the percolation tube above the soil was first displaced by leaving the stopper loose when the gas was first applied. The stopper was then fitted tightly and the gas passed through the soil for $3\frac{1}{2}$ minutes. As quickly as possible, a thin cork disk was placed on the soil surface to receive the impact of the water. The percolation tubes were then filled with water by means of a rubber ear syringe and then connected to a constant-level supply bottle as previously described (2).

EXPERIMENTAL RESULTS AND DISCUSSION

For simplicity, the soils through which the CO_2 was passed are referred to as "treated" and those not receiving CO_2 as "untreated." The results are summarized in table 1, which gives the permeabilities of both the treated and the untreated soils at various times during the test. For the treated soils, the permeabilities at the beginning (called the initial permeability), at 24 and 48 hours, and at 10 days are given. For the untreated soils, the initial permeability, the minimum rate prior to the increase accompanying the elimination of the entrapped air, the maximum rate, and the rate after 10 days of percolation are given. The time in days required for the occurrence of the minimum and maximum rates is also given. These points are sufficient to define roughly the permeability-time graphs as illustrated with selected soils in figures 1 and 2.

With one exception, the initial permeability of the treated soils was the maximum recorded. (The permeability of the Hesperia sandy loam, number 453, reached a maximum of 7.02 cm. per hour in approximately 2 hours.) Subsequently, the permeabilities decreased rapidly for some of the soils, and gradually for others, so that in 10 days the rates ranged from 2 to 84 per cent of the initial rate. This behavior was characteristic for all soils treated with CO_2 but was markedly different from that of the untreated soils.

During the initial phase of the test, the permeability of the untreated soils, with one exception decreased to a minimum, which in two instances (numbers 397 and 68) was less than 10 per cent of the initial rate. In all cases, the maximum permeability was attained in 2 to 19 days after the test was started, but in most cases it was within the 10-day period. In two instances (indicated by footnotes), the rate was still decreasing after 10 days, and in four instances it was increasing at 10 days, reaching maxima at 15 to 19 days.

Figure 1 shows typical permeability-time relations for two surface soils. The initial permeability of the treated Fort Collins loam was about four times that of the untreated soil, and for Yolo fine sandy loam the corresponding ratio was approximately 7:1. In both instances, the permeability of the treated soil dropped to less than half the initial rate in 24 hours. The permeability of the untreated soils also dropped during the initial period, but then it increased

sharply as the entrapped air was dissolved in the percolating water. The maximum rates for the untreated soils were more than three times their initial rates, and more than six times their minimum rates but appreciably less than the initial rates for the treated soils. In general, the results on the other surface soils were similar.

TABLE 1
Effect of displacing soil-air with CO_2 on the permeability of soil samples

LAB. NO.	DEPTH	SOIL	PERMEABILITY OF CO₂-TREATED SOILS					PERMEABILITY OF UNTREATED SOILS					
			Initial	24 hours	48 hours	10 days		Initial	Minimum		Maximum		10 days
	ft.		*cm./hr.*	*cm./hr.*	*cm./hr.*	*cm./hr.*	*per cent**	*cm./hr.*	*cm./hr.*	*days*	*cm./hr.*	*days*	*cm./hr.*
		Exeter											
393	0–0.6	loamy sand	0.97	0.32	0.22	0.12	12	0.32	0.18	3	0.32	5	0.22
394	0.6–0.9	loamy sand	0.83	0.59	0.46	0.20	24	0.30	0.098	2	0.75	7	0.35
395	0.9–1.4	loamy sand	1.25	0.73	0.61	0.50	40	0.40	0.096	5	1.40	19	0.17†
396	1.4–1.9	sandy loam	1.74	0.89	0.82	0.60	34	0.32	0.083	7	1.77	15	0.12†
397	1.9–2.2	sandy clay loam	2.31	0.17	0.12	0.04	2	0.17	0.013	18	....	..	0.017‡
398	2.2–2.5	sandy clay loam	7.60	6.50	5.70	3.80	50	2.14	1.98	1	9.15	4	5.28
399	2.5–3.2	sandy loam	4.05	3.59	3.90	3.41	84	1.05	1.05	0	4.32	7	4.09
420	0–0.7	loamy sand	1.92	....	0.46	0.26	14	0.59	0.13	3	0.76	7	0.53
421	0.7–1.0	sandy loam	0.96	0.72	0.72	0.51	53	0.26	0.24	3	0.84	15	0.40†
422	1.0–1.5	loamy sand	3.52	....	1.78	0.48	14	0.71	0.64	1	1.84	4	0.65
423	1.5–2.0	sandy loam	7.77	5.96	5.54	3.40	44	1.75	1.51	0	6.97	6	5.80
424A	2.0–2.4	sandy loam	7.41	5.73	5.44	3.63	49	1.77	1.66	0	7.69	3	5.61
424B	2.4–2.8	sandy loam	12.28	11.24	10.24	6.92	56	3.16	2.76	0	14.60	2	8.75
424C	2.8–3.1	sandy loam	18.60	16.28	14.95	12.13	65	5.34	4.68	0	20.80	3	15.11
		Hesperia											
453	0–0.5	sandy loam	6.60	4.98	4.44	3.16	48	2.87	2.30	2	4.00	4	3.20
85	0.2–0.7	Reagan clay loam	3.41	1.00	0.62	0.30	9	0.59	0.43	2	0.76	5	0.42
		Yolo fine											
75	0.2–0.5	sandy loam	4.35	1.70	1.22	0.61	14	0.62	0.33	3	2.03	7	1.63
		Glendale											
79	0.2–0.5	silt loam	0.94	0.35	0.25	0.12	13	0.28	0.066	7	0.37	19	0.071†
83	0–0.5	Fort Collins loam	6.49	2.12	1.77	1.04	16	1.64	0.81	1	5.05	3	2.65
		Vale sandy											
68	0.2–0.5	clay loam	2.02	1.00	0.89	0.23	11	0.75	0.011§	60	....	..	0.043‡

* Of initial.
† Permeability increasing at 10 days; entrapped air not eliminated.
‡ Permeability still decreasing at 10 days; entrapped air not eliminated.
§ Permeability still decreasing at 60 days; entrapped air not eliminated.

Figure 2 shows the permeability-time relations for three Exeter subsoil samples taken from a single sampling site. The maximum rates of the untreated samples of this soil were higher than the initial rates for the treated samples. The decrease in permeability of the treated subsoil material was less rapid than for the treated surface soils, with the exception of Exeter 397 (not shown). Exeter soils 397 and 398 from depths of 1.9–2.2 and 2.2–2.5 feet, respectively, were very similar in texture, appearance, and apparent density, but chemical analyses indicated that soil 397 had a higher percentage of exchangeable sodium, which undoubtedly resulted in an increase in dispersion. During the first 24 hours, the permeability of the treated Exeter 397 decreased from 2.31 to 0.17 cm. per hour,
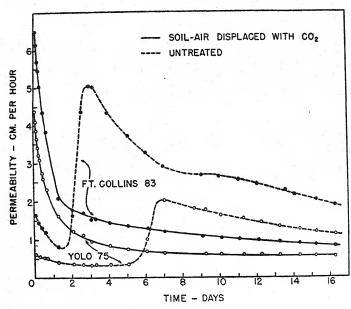
FIG. 1. TYPICAL PERMEABILITY-TIME CURVES FOR TWO SURFACE SOILS, SHOWING
DIFFERENCES IN CHARACTERISTICS FOR CO_2-TREATED AND
UNTREATED SAMPLES
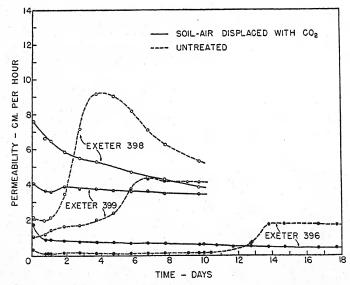
FIG. 2. EFFECT OF CO_2 DISPLACEMENT OF AIR ON THE PERMEABILITY OF SUBSOIL MATERIAL
FROM VARIOUS DEPTHS IN AN EXETER SANDY LOAM PROFILE

while the same soil, untreated, decreased from 0.17 to 0.043. The test on the
untreated sample of this soil was discontinued after 21 days while there was an
appreciable amount of entrapped air present.

Exeter soils 420 to 424C were from the same general location as the other Exeter soils but were from an experimental water-spreading pond through which several hundred feet of water had percolated prior to time of sampling. In general, these samples were more permeable than those from corresponding depths outside the pond.

The effect of CO_2 on infiltration of the water into the soil was striking. The time required for the untreated soils to wet and begin to drip averaged more than twice that for the treated soils, the ratios for the different soils varying from 1.7 to 9.0. The ratio was highest for Exeter 397.

Ten days after the inception of percolation, the untreated soils had higher permeability rates than those treated with CO_2, with the exception of those which had not yet reached their maximum rate. The data suggest that when air is entrapped in the pores of the soil and held there for several days during percolation, these pores become more or less stabilized and remain open for the passage of water after the air is dissolved, whereas when the soil is completely saturated at the beginning of the test, the pores are less stable, apparently, and the aggregates forming them probably disintegrate somewhat and partially fill the pores with dispersed particles, with the result that the permeability of the soil decreases more rapidly. Similar results were noted in earlier tests in which air was removed by evacuation (2).

Conductance ($K \times 10^5$ at 25°C.) was determined on the leachate from some of the soils. In most instances, the first sample of leachate (approximately 50 ml.) from the treated soils had an appreciably higher conductance then the leachate from the untreated soils. Subsequent samples from the treated soils had slightly lower conductances than those from the untreated soils. The increased CO_2 content of the initial leachate undoubtedly brought into solution additional electrolytes, but the effect was temporary and the conductance of the leachate from both the treated and the untreated soils quickly approached that of tap water. The principal changes in permeability occurred after the conductance of the leachates had become stabilized. Samples of leachate from the Hesperia soil 453 were titrated for bicarbonate ion. The bicarbonate content of the first 50-ml. sample of leachate from the treated soil was approximately twice that of the untreated soil, but for subsequent samples the differences were not significant. The maximum permeability of the treated soil occurred while the fourth sample was being collected, at which time the leachate composition was essentially that of the tap water. There was no indication that the use of CO_2 for displacing the air produced any chemical effect that influenced the permeability.

Displacement of soil-air with CO_2 before wetting is simple and brings about the complete saturation of a soil in a very short time, allowing the permeability of the saturated soil to be determined without waiting several days for the entrapped air to dissolve. Since immediate complete saturation of the soil appears, however, to result in a more rapid and pronounced decrease in the permeability of the soil, it is difficult to compare permeabilities of CO_2-treated and untreated soils. For this reason, the technique described here may not be useful for all purposes but is well suited for specific purposes, such as determination of the permeability

of subsoils in connection with drainage studies, especially fine sands which have essentially no structure. For such tests, the saving in time by using CO_2 is considerable and will allow several times as many tests to be made in a given length of time with the same equipment. For example, Aronovici and Donnan (1) report that in their drainage studies routine tests on very fine sands are run for 100 to 400 hours in order to obtain maximum rates.

SUMMARY AND CONCLUSIONS

The experiment reported herein indicates that the air which is normally entrapped within a soil upon wetting can be eliminated by displacement with CO_2 prior to wetting. When this is done, the permeability is a maximum at the beginning of the test or shortly thereafter. Where it is desirable to determine the permeability rates for complete saturation, this technique eliminates the necessity of long-time tests.

For subsoils, sands, and structureless materials, in which the decrease in permeability is very gradual, the initial permeabilities of the CO_2-treated samples are approximately the same as the maximum permeabilities for the untreated samples, which are obtained only after a period of a few to many days. In surface soils, however, the initial rates for the CO_2-treated samples are appreciably higher than the maximum rates reached by the untreated samples.

The technique described here appears to have special time-saving value in connection with permeability tests for drainage studies and other engineering purposes where the permeability of completely saturated materials is desired.

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TITRIMETRIC DETERMINATION OF SULFATE IN NATURAL WATERS AND SOIL EXTRACTS

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In the course of routine investigations of natural and irrigation waters and other miscellaneous solutions, a rapid method of analysis for sulfate is frequently desirable. The analyst often finds, however, that the only satisfactory generally accepted method is that which involves the precipitation of sulfate as the barium salt and a subsequent gravimetric determination of this constituent (5).

Because it was often necessary to determine sulfate gravimetrically at the expense of much-needed time, it seemed that a determination of this constituent by precipitation with an acid solution of barium chromate, removal of excess barium by alkalization, and analysis of excess chromate titrimetrically with thiosulfate might prove to be a feasible analytical procedure.[2] Based on somewhat analogous series of reactions, attempts have been made to determine sulfate (1, 2, 3, 4, 6, 9). In most instances, however, it has been established that such methods are inaccurate to some degree and present many limitations.

Manov and Kirk (7) pointed out that constant irregularities have been observed in many of the chromate methods reported in the literature and that the absolute error is usually found to be 5 per cent or more. These investigators attributed such inconsistencies to oxygen errors involved in the oxidation of iodide to iodine, time of digestion of the barium chromate precipitate, and reduction of dichromate by chloride in acid solution. They concluded that no completely satisfactory method for analysis of sulfate with chromate existed at the time of their writing. Meldrum *et al.* (8) observed that inconsistencies in analytical results occur if conditions are not carefully controlled. These investigators found that coprecipitation reactions were responsible for the deviations from actual sulfate content introduced into the experimental results. Their observations indicated that the quantity of chromate coprecipitated varied directly with increasing acid concentration and rate of addition of the precipitant. The amount of coprecipitation was also found to be dependent on the chromate-sulfate ratio and the time of digestion.

As a consequence of repeated experimentation, it has been observed by the author that analysis of residual chromate left in solution after simultaneous removal of barium chromate and barium sulfate seldom yields results which coincide with the absolute concentration of sulfate originally present. Extensive investigations indicate conclusively, however, that with proper control of the

procedure, results established by titrimetric analysis are a function of the original sulfate content within relatively wide limits. Consequently, it has been found possible to plot the apparent sulfate content on a series of standard sulfate solutions against the actual sulfate content. This relationship is delineated in the
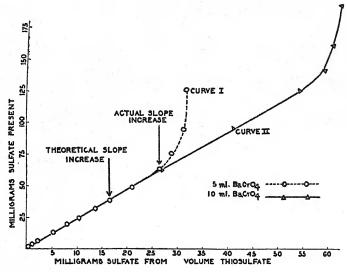
FIG. 1. RELATIONSHIP BETWEEN ACTUAL AND APPARENT SULFATE CONTENT

form of rectilinear curves in figure 1, from which the concentration of this constituent can be determined by graphic comparison or by formula.

METHOD

Reagents

0.1724 N sodium thiosulfate
KI (solution of 40 gm. per 100 ml. H_2O)
Phenolphthalein (0.2 per cent alcoholic solution)
$BaCrO_4$ (10 gm. per 500 ml. 0.8 N HCl) 5 N NaOH
Soluble starch solution (1 per cent)
Standard H_2SO_4 solutions (1,500 and 6,000 mgm. per liter sulfate)
0.5 N HCl
1-1 HCl

Standard curve

In order to evaluate the relationship between the amount of sulfate determined by reduction of excess chromate with thiosulfate and the actual sulfate content, two standard solutions (1,500 and 6,000 mgm. per liter sulfate) were prepared from sulfuric acid and standardized gravimetrically as the barium salt. Aliquots of these solutions were analyzed by the method described in the following section, and the results obtained were plotted against the actual amounts of sulfate present (fig. 1). A graph of the original sulfate contents as a function of the volumes

of thiosulfate was desirable (fig. 2) in order to eliminate the necessity of calculating a sulfate value from the thiosulfate titer before comparisons could be made. By formulation, this curve was used as a basis for the analysis of synthetic composites and natural waters (tables 3 and 4).
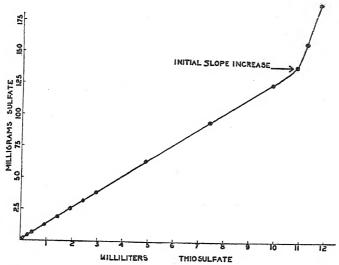
FIG. 2. STANDARD CURVE FOR DETERMINATION OF SULFATE CONTENT FROM VOLUME THIOSULFATE

Procedure

A sample of water containing less than 140 mgm. sulfate is diluted to 100 ml. in a 250-ml. Erlenmeyer flask. HCl (0.5 N) is added dropwise until the mixture is acid to phenolphthalein. An excess of 10 to 15 drops is added, and the solution is boiled rapidly for 2 minutes to eliminate carbonate and bicarbonate.[3] Then 5 N NaOH is introduced dropwise until the solution is just alkaline to phenolphthalein, and 10 ml. barium chromate reagent is added. The solution is rapidly heated and digested slightly below the boiling point for 15 minutes on an electric hot plate. It is removed from the heater and two drops of phenolphthalein added to the hot solution, followed by dropwise addition of 5 N NaOH to one drop in excess of the indicator change. The solution is brought rapidly to boiling and digested slightly below the boiling point. The total heating period should be exactly 10 minutes. The solution is filtered rapidly through a quantitative filter paper into a 250-ml. Erlenmeyer flask. The flask is washed with 10 ml. of water, and finally the filter paper and contents are washed with a second 10 ml. of water. The filtrate is rapidly cooled under the tap to room temperature, and

[3] It is desirable at this point to remove anions such as carbonate and bicarbonate. At a later stage in the determination, liberation of these constituents in the form of CO_2 with a corresponding change in the hydrogen-ion concentration will affect the optimum conditions necessary for the initial complete precipitation of barium sulfate.

5 ml. 1-1 HCl is added, followed by 5 ml. of KI reagent. The solution is allowed to stand in the dark for 3 minutes. Then 5 ml. of soluble starch reagent is introduced,[4] and the solution is titrated with standardized thiosulfate reagent to the disappearance of the blue starch-iodide complex.[5] From the volume of thiosulfate used, the sulfate content is obtained by graphic comparison or by calculation from the formula.

<center>DISCUSSION</center>

Water aliquot

In order to employ this method of sulfate analysis, a rapid semiquantitative determination of the approximate sulfate content of mineral waters is desirable. Several milliliters of 10 per cent barium chloride is introduced into an aliquot of the water to be analyzed. The density of the precipitate subsequently formed can be compared with a set of turbidity standards. As a result, it is possible to choose an aliquot of appropriate strength for the more exact determination.

Chromate reagent

Ten grams of freshly prepared barium chromate was dissolved in 500 ml. of 0.8 N HCl. Under the conditions of this determination, the barium chromate concentration is of sufficient strength to account quantitatively for the presence of approximately 5 to 140 mgm. of sulfate. The pH is such that the solution to be analyzed will have a hydrogen-ion concentration between 0.05 N and 0.1 N. Optimum conditions for quantitative precipitation of sulfate are thus attained (5).

Phenolphthalein

The volume of indicator introduced prior to the 10-minute alkaline digestion period must be kept constant throughout all determinations. Dichromate is subject to reduction with simultaneous oxidation of C_2H_5OH to CH_3CHO, and appreciable error can be introduced if an excess of indicator is added at this point (table 1).

Time of heating

It has been suggested in the procedure for analysis that the alkaline solution be digested for 10 minutes. Actually, a 5- or 15-minute heating period might be permissible, but this interval must equal that used in the determination of the standard curve. Slight deviations occur in the thiosulfate titer when the digestion period is altered.

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[4] When the density of the brown iodine color is indicative of a titration value appreciably higher than 1 to 2 ml., sodium thiosulfate should be introduced first to within 1 ml. of the end-point, followed by 5 ml. of starch, and the titration completed.

[5] A microburette is necessary for the determination of low concentrations of sulfate, which yield titration values in the vicinity of 0 to 10 ml. Also, a weaker solution of thiosulfate (from 0.05 to 0.1 N) can be used to advantage.

Washing

From a theoretical point of view, 100 ml. of neutral CO_2-free water can dissolve 0.4 mgm. of barium chromate at 20°C. Consequently, it was suspected that excessive washing of the precipitate might account for deviations which were obtained when this factor was not controlled. Table 2 illustrates the effect of different volumes of wash water on the accuracy of this determination. Consistency in the volume of wash water is necessary throughout the course of analysis.

TABLE 1

Effect of variation in volume of alcoholic phenolphthalein on sulfate determination

SULFATE PRESENT	VOLUME PHENOLPHTHALEIN	VOLUME THIOSULFATE	VOLUME THIOSULFATE CORRECTED FOR BLANK	SULFATE CALCULATED BY FORMULA	DEVIATION FROM ORIGINAL SULFATE CONTENT
mgm.		ml.	ml.	mgm.	per cent
0.0	2 drops	0.4	0.0	0.0	. . . .
31.9	2 drops	2.82	2.42	32.0	0.3
31.9	10 drops	2.60	2.20	29.3	8.2
31.9	1 ml.	1.22	0.80	11.3	64.6
31.9	3 ml.	0.40	. . . .	. . . .	. . . .
31.9	5 ml.	0.15	. . . .	. . . .	. . . .

TABLE 2

Effect of variation in volume of wash water on sulfate determination

SULFATE PRESENT	VOLUME WATER	VOLUME THIOSULFATE	VOLUME THIOSULFATE CORRECTED FOR BLANK	SULFATE CALCULATED BY FORMULA	DEVIATION FROM ORIGINAL SULFATE CONTENT
mgm.	ml.	ml.	ml.	mgm.	per cent
0.0	20	0.4	0.0	. . . .	. . .
31.9	20	2.82	2.42	32.1	0.6
31.9	40	2.82	2.42	32.1	0.6
31.9	60	2.85	2.45	32.5	1.9
31.9	80	2.85	2.45	32.5	1.9
31.9	100	2.88	2.48	32.8	2.8
31.9	200	2.92	2.51	33.2	4.1

Effect of other ions on precipitation of sulfate

The constituents generally occurring in waters, in addition to sulfate, are calcium, magnesium, sodium, potassium, chloride, nitrate, carbonate, and bicarbonate. Investigations have shown that these do not interfere to an appreciable degree with the outlined method of analysis (table 3). Other ions, such as phosphate, ferric, and borate, generally occur only in insignificant quantities.

Discussion of standard curves

The curves plotted from experimental data (figs. 1 and 2) have been used for computing the quantities of sulfate in synthetic composites and natural waters.

By calculation, a 5-ml. aliquot of barium chromate, equivalent to 100 mgm. of this compound, should account for the precipitation of approximately 38 mgm. of sulfate (if complete precipitation of BaSO$_4$ took place, based on the actual barium content of the solution). The standard curve, however, does not show an increased slope until a point is reached at approximately 65 mgm. of sulfate

TABLE 3

Analysis of synthetic solutions

Sodium, potassium, and nitrate present in excess of 100 mgm. in all cases

CALCIUM	MAGNESIUM	SULFATE PRESENT	VOLUME THIO-SULFATE*	VOLUME THIOSULFATE CORRECTED FOR BLANK	SULFATE CALCULATED BY FORMULA	DEVIATION FROM ORIGINAL SULFATE CONTENT
mgm.	*mgm.*	*mgm.*	*ml.*	*ml.*	*mgm.*	*per cent*
...	...	....	0.40	....	....	...
25	25	6.4	0.82	0.42	6.5	1.6
50	50	6.4	0.81	0.41	6.4	0.0
100	100	6.4	0.81	0.41	6.4	0.0
25	25	25.5	2.31	1.91	25.6	0.4
50	50	25.5	2.30	1.90	25.4	0.4
100	100	25.5	2.32	1.92	25.7	0.8
50	50	95.8	7.82	7.42	96.1	0.3
75	75	95.8	7.82	7.42	96.1	0.3
100	100	95.8	7.85	7.45	96.5	0.7

* Average of two determinations.

TABLE 4

Analysis of some waters

SULFATE BY GRAVIMETRIC ANALYSIS	ALIQUOT TAKEN	SULFATE PRESENT	VOLUME THIO-SULFATE*	VOLUME THIOSULFATE CORRECTED FOR BLANK	SULFATE CALCULATED BY FORMULA	DEVIATION FROM ORIGINAL SULFATE CONTENT, DETERMINED GRAVIMETRICALLY
mgm./l.	*ml.*	*mgm.*	*ml.*	*ml.*	*mgm.*	*per cent*
...	...	....	0.40	....	....	...
250	100	25.0	2.29	1.89	25.3	1.2
474	100	47.4	4.03	3.63	47.6	0.4
162	100	16.2	1.59	1.19	16.3	0.6
481	100	48.1	4.08	3.68	48.2	0.2
882	100	88.2	7.14	6.74	87.4	0.9

* Average of two determinations.

(fig. 1, curve I). If 10 ml. of barium chromate solution is used, a deviation from the linear slope occurs at approximately 140 mgm. of sulfate. Consequently, an addition of 100 mgm. of available barium chromate yields a proportional increase in the length of the linear segment of the curve. Apparently, under the conditions of the analysis, the competition for barium between an excess of chromate and a limited amount of sulfate in solution results in an equilibrium which does not allow complete precipitation of sulfate. This results in a low estimation for

the sulfate content of the solution (by calculation from the thiosulfate titer). Within limits (6 to 140 mgm. original sulfate content), however, this relationship introduced a constant factor which allows for a correlation between the actual and apparent sulfate concentrations.

Equation for calculation of sulfate content

It is apparent from the curve in figure 2 that, within limits, a linear relationship exists between original sulfate content and volume of thiosulfate. In order to eliminate the necessity of a sulfate determination by graphic comparison, it was felt that an equation for calculation of sulfate content would be desirable. Consequently, the data were analyzed in order to determine the practicability of such a correlation. It was found that the relationship could be best approximated by the equation $y = 12.8x + 1.1$, where $y = $ mgm. sulfate and $x = $ ml. thiosulfate. The method was found to be accurate to better than 1 per cent for initial sulfate contents of 6 to 140 mgm. of sulfate. With an initial content of 3 to 6 mgm. sulfate, the error involved is approximately 3 per cent.

The minimum limits of sensitivity are such that small amounts of sulfate can be rapidly determined. The uniformity of the procedure indicates that coprecipitation and occlusion of foreign material, which often account for erroneous results in gravimetric analysis, are not responsible for inconsistencies in this determination. A satisfactory analysis of such small amounts of this constituent can seldom be obtained by the ordinary procedures of gravimetric analysis.

SUMMARY

An empirical, rapid method of analysis for sulfate in waters is presented. Sulfate is precipitated with an acid solution of barium chromate, excess barium is eliminated by alkalization, and residual chromate is determined titrimetrically with thiosulfate. The actual sulfate content is a function of the thiosulfate titer, and evaluation of the sulfate concentration can be made either by comparison with a standard curve or by formula.

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ABSORPTION OF CALCIUM BY PEANUTS FROM KAOLIN AND BENTONITE AT VARYING LEVELS OF CALCIUM[1]

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The specific influence that the type of colloidal material exerts upon mineral uptake by plants has not been thoroughly investigated. Elgabaly, Jenny, and Overstreet (6) have found this factor to be of importance in the absorption of zinc and potassium by barley roots. In a previous study by the authors (7), where cotton and soybeans were used as the indicator crops, it was found that the availability of Ca was greater from soils of the kaolinitic systems than it was from those high in montmorillonitic material. Similar results with soybeans grown on colloids representing the 1:1 and 2:1 lattice types of minerals have been recently reported by Allaway (1).

In pursuing the studies on the effect of type of clay on the release of Ca, it was considered desirable to introduce certain modifications in the technique previously employed (7) to measure this phenomenon. Two major changes were introduced: (*a*) relatively pure systems of clay material of the 2:1 and 1:1 types were used instead of soils high in one or the other, and (*b*) the peanut plant with a known high Ca requirement for fruit development was employed.

It was already known from other work (4) that for proper filling of fruit the large type peanut has a relatively high Ca requirement, and that Ca supplied to the soil in which the fruit develop is effective in promoting well-filled nuts. Furthermore, it is known (5) that the Ca content of the peanut shell reflects differences in Ca supply to the peanut fruit. It was thought, therefore, that the two criteria, records on fruit development and the Ca content of the shell, would provide a sensitive measure of Ca release from the colloidal systems.

A further advantage of this technique in which colloid variables were supplied only to the fruiting medium (as described below) was thought to lie in at least partial elimination of secondary effects, such as phosphorus supply, cation competition, and aeration, that the different colloidal systems might have on plant growth.

The initial study with these systems was conducted in 1943 and with certain modifications the work was repeated in 1944. The results of the 2 years' investigations are presented separately.

MATERIALS AND METHODS

Colloidal systems

Bentonite (Volclay) represented the montmorillonitic type of colloid. The kaolinitic material used was "Kamec Kaolin." Its cation adsorption capacity

was 8.2 m.e. per 100 gm., and the differential thermal curve showed it to be predominantly kaolinite with less than 1 per cent gibbsite.

Hydrogen-saturated clays were prepared by placing the colloidal material in 5-gallon bottles or in barrels of about 50-gallon capacity with distilled water and adding sufficient HCl to supply twice the symmetry concentration. After settling, the supernatant liquid was decanted, water was added, and HCl at 1 symmetry. This was repeated, and subsequently the colloid was treated with water only, until the supernatant liquid gave no test for Cl ions.

Known amounts of the suspensions were then placed in 4-gallon pots, and known increments of a saturated solution of $Ca(OH)_2$ were added to supply Ca at

TABLE 1

Cation adsorption capacity and calcium levels of colloid: sand mixtures

KAOLIN				BENTONITE			
1943 investigation		1944 investigation		1943 investigation		1944 investigation	
Calcium on colloid							
m.e.	per cent	m.e.	per cent	m.e.	per cent	m.e.	per cent
Cation adsorption capacity 2.4		cation adsorption capacity 2.4		cation adsorption capacity 4.8		cation adsorption capacity 2.4	
0.39	16.2	0.39	16.2	1.31	27.6	0.66	27.5
0.74	30.8	0.74	30.8	1.75	36.5	0.88	36.6
1.33	55.4	1.33	55.4	2.75	57.3	1.38	57.5
1.97	82.1	1.97	82.1	3.84	80.0	1.92	80.0
2.37	98.8	2.37	98.8	4.75	99.0	2.38	99.1
Cation adsorption capacity 1.4		cation adsorption capacity 0.8		cation adsorption capacity 2.8		cation adsorption capacity 0.8	
0.17	12.1	0.09	11.2	0.67	23.9	0.09	11.2
0.29	20.7	0.15	18.8	1.02	36.5	0.17	21.2
0.68	48.6	0.34	42.5	1.46	52.2	0.26	32.5
1.06	75.7	0.53	66.2	1.86	66.4	0.37	46.3
1.25	89.3	0.63	78.8	2.55	91.1	0.47	58.8
						0.64	80.0

varying degrees of Ca saturation. The suspensions were stirred frequently for 6 days, after which pure quartz sand was added and mixed. Sand was added to give different cation-adsorption capacities. The clay-sand mixtures were brought to dryness in a drying barn at a temperature of 40 to 50°C. The dry materials were then crushed, mixed, and finally placed in the wooden flats which served as the fruiting medium, as described below. At the end of the 1943 growing season the cation-adsorption capacity and the exchangeable Ca were determined by the $BaCl_2$-triethanolamine procedure (8). The results are reported in table 1.

Cultural methods[2]

A bulk sample of Ruston sand surface soil known to produce poor quality peanuts in the field was placed in a wooden frame, 6 feet long, 6 inches wide, and

[2] The technique used to separate the rooting medium from the fruiting medium was a modification of that diagrammatically described by Burkhart and Collins (3, p. 279).

8 inches deep. These troughs were fastened securely in concrete frames on the campus at Raleigh, N. C., in such a way that the surface of the soil was approximately at ground level. Along each side of this trough were placed wooden flats, 3 inches deep, 9 inches wide, and 12 inches long. The runners of four plants (two in 1943) were trained so that most of their fruits grew in the pair of boxes containing the colloid:sand mixtures.

Two pairs of fruiting medium boxes were used for each treatment, and data on each side of the plants were then taken separately. The results on fruit quality were evaluated according to a procedure described in detail elsewhere (4). All the fruits were detached from the vines and so classified that it was possible to calculate the percentage of the ovarian cavities containing well-developed kernels.

Calcium determinations were made on shells that contained one or two well-developed kernels. The macromethod of the A.O.A.C. (2) was employed.

In the 1943 experiment, plants were grown from seed planted on May 19 and were harvested on October 27. In 1944, seeds already sprouted were set out on June 4, and the harvest was on October 20. The peanut Jumbo Runner variety (*Arachis hypoagaea* L.) was used in both studies.

In 1943, the moisture was maintained by additions of tap water to the rooting medium and distilled water to the fruiting medium, whereas distilled water was used for both media the following year.

RESULTS AND DISCUSSION[3]

· *1943 investigation*

In figure 1 are presented the data obtained in 1943. From the standpoint of shell composition, the following facts are readily apparent: (*a*) for comparable calcium levels, invariably more Ca was absorbed from the kaolinitic systems than from the montmorillonitic; (*b*) the uptake of Ca increased with increases in either absolute Ca level or percentage Ca saturation in any one system; (*c*) the uptake of Ca increased sharply with additional increments of this element of the kaolinitic system and was only moderately increased in the montmorillonitic colloid. For example, an increase of 0.8 m.e. Ca on the colloid (from 0.8 to 1.6) raised the Ca content of shells in the kaolinitic system approximately 8 m.e. per 100 gm. and in the montmorillonitic system less than 3 m.e. (fig. 1). At low levels of Ca these differences tended to become smaller.

From the standpoint of fruit development, the 1943 results showed that kernels developed quite normally in all systems. The levels of Ca selected were probably too high to permit the use of this criterion as a measure of Ca release. In view of this fact, certain adjustments were made in concentrations before the 1944 study was begun.

[3] In interpreting the results, it should be noted that no differential treatments were used which would affect vegetative development of the roots and tops. There were some differences in the total vegetation and, hence, differences in the number of gynophores present. These variations, however, were not related to Ca differentials made to the fruiting medium only. The Ca contents of the peanut shells serve, therefore, as a reliable criteria for relative Ca availability.

1944 investigation

The sand-clay mixtures were stored until the spring of 1944, when the following adjustments were made: (*a*) kaolin with a cation-adsorption capacity of 2.4 was not further diluted, (*b*) kaolin 1.4 was diluted with sand to give 0.8 m.e., (*c*) bentonite 4.8 was diluted to give 2.4, and (*d*) bentonite 2.8 was diluted to give 0.8. (The bentonite culture medium containing 0.09 m.e. Ca was made fresh in 1944.) No additional Ca was added, and dilutions were made with acid-washed quartz sand. In interpreting the results of this study, it should be kept in mind
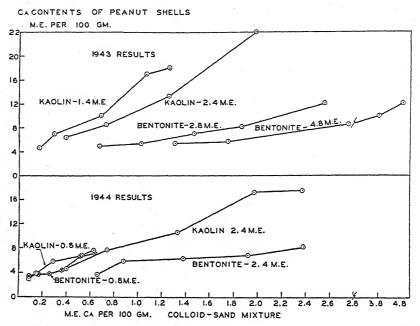
FIG. 1. CALCIUM CONTENT OF PEANUT SHELLS AS AFFECTED BY TYPE OF COLLOID, CATION ADSORPTION CAPACITY, AND CALCIUM LEVEL

The cation-adsorption capacity of the clay:sand mixtures follows the name of the type of clay.

that the systems had been in equilibrium for approximately 1 year at the time of planting, and that in 1944 distilled water was used exclusively.

From the standpoint of Ca content of peanut shells, it is important to note, from the results presented in figure 1, that the relationship between kaolin and bentonite in the "high cation-adsorption capacity" systems is essentially the same as that found by the 1943 studies, that is, more Ca was found in the shells produced in the kaolinitic system, particularly at the high concentrations. When the systems were diluted to provide mixtures of only 0.8 m.e. cation-adsorption capacity, the differences in behavior between the two types of colloidal material tended to disappear. It will be recalled that this tendency had already been indicated by the first year's work.

It should be noted further that in the kaolinitic system there was little difference in the Ca content of the shells when, for example, 0.63 m.e. Ca was supplied at approximately 79 per cent in the 0.8 m.e. series or at 26 per cent saturation in the 2.4 m.e. series. On the other hand, in the bentonite system, the Ca content of the shells was influenced markedly by the percentage Ca saturation of the clay medium. For example at 80 per cent saturation in the 0.8 m.e. series, 0.64 m.e. Ca resulted in shells containing over 7 m.e. Ca per 100 gm., whereas the same amount of Ca in the soil, but at 27 per cent saturation in the 2.4 m.e. series resulted in shells containing only half this quantity.
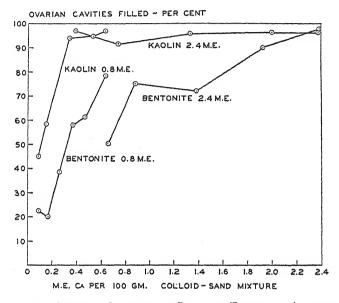
FIG. 2. PERCENTAGE OVARIAN CAVITIES OF PEANUTS FILLED AS AFFECTED BY TYPE OF COLLOID, CATION-ADSORPTION CAPACITY, AND CALCIUM LEVEL

From the standpoint of fruit development, it is evident from the data in figure 2 that the Ca concentrations selected in 1944 were such as to provide a wide range in fruit quality. In the kaolinitic systems almost 95 per cent of the ovarian cavities were filled with only 0.34 m.e. Ca per 100 gm. of medium. This was true when it was supplied in the 0.8 m.e. series at 42.5 per cent Ca saturation or in the 2.4 m.e. series at 16.2 per cent Ca saturation. This draws attention to the fact that the absolute quantity of Ca for the kaolinitic system is of relatively greater importance than is percentage Ca saturation.

On the other hand, in the bentonite series, approximately 79 per cent of the ovarian cavities were filled with a supply of 0.65 m.e. Ca when it occurred in the highly saturated systems (80 per cent saturation 0.8 m.e. cation-adsorption capacity), whereas with essentially the same amount of Ca but with the system only 27.5 per cent saturated (2.4 m.e. series) only 50.4 per cent of the ovarian cavities were filled. It is of interest that in only one of the bentonite systems,

namely, 99 per cent Ca-saturated to supply 2.38 m.e. Ca, was as good fruit produced as in the kaolinitic system.

On the basis of the results reported in this and in the previous paper (7), it is evident that by means of widely different criteria, namely, Ca content of peanut shells, measurement of fruit quality, yield and uptake of Ca by cotton and soybeans, the effect of type of colloid upon the release of Ca is evidenced. This is true whether the exchange minerals are used in relatively pure form or as mixtures in soil.

SUMMARY

An investigation was undertaken to measure the uptake of Ca by peanuts, as affected by the type of soil colloid, at varying levels of exchangeable Ca. Relatively pure colloidal material of the 1:1 and 2:1 lattice types was used. In all cases, variations in adsorption capacity were provided by dilutions of the material with quartz sand. Criteria to measure the release of bases from these systems were the Ca content of shells and the fruit quality records of peanuts.

In all systems the uptake of Ca increased with increasing Ca levels. The Ca contents of peanut shells produced in the kaolinitic systems were higher than those in the bentonite media. This difference due to type of colloid was more pronounced at high degrees of Ca saturation and at the higher cation adsorption capacity levels (2.4 m.e. per 100 gm.).

Uptake of Ca from the kaolinitic systems was more directly related to total Ca present than to degree of saturation. In the montmorillonitic systems, on the other hand, absorption was more directly related to percentage Ca saturation than to total amount.

The effect of type of clay on release of Ca was evidenced also by the quality of fruit produced. In the case of the kaolinitic type of colloid, fruits of good quality were obtained even at relatively low Ca levels. In the bentonitic system larger amounts of Ca, at high degrees of saturation, were required to produce similar fruit quality.

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ARRANGEMENT OF SOIL SERIES AND TYPES ACCORDING TO FUNCTIONS OF SOIL-FORMING FACTORS

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In the United States, thousands of soil series and types have been mapped and described in great detail. The problem of classifying this huge array of soil units either on a state-wide or a national basis is of concern to every soil surveyor and pedologist. The writer believes that a grouping of soil series and types in terms of functions of soil-forming factors has certain merits, for it emphasizes a logical interlacing of soil units and is amenable to geographic expression. The purpose of this paper is to present the theory of this approach and to give practical applications.

THE FIVE PEDOLOGIC FUNCTIONS

The general equation of soil-forming factors may be expressed as follows:

$$s = f(cl, o, r, p, t, \ldots) \tag{1}$$

As defined by the writer, the symbols have the following significance:

s = any soil property such as color, reaction, clay content, nitrogen content, or lime. These properties are treated as dependent variables.

f = symbol for "function of," or "dependent on."

cl = air climate (environmental climate).

o = species of organisms and their frequencies, referring to seeds rather than actual growth of plants. (For further details, see section on "Biosequences.")

r = topography or shape of the boundry between soil and environment; it also includes certain hydrologic features.

p = parent material, defined as the state of the soil at the soil formation time 0; it may or may not be identical with the C horizon.

t = period of soil formation (age of soil).

In the above formulation, cl, o, r, p, and t have been given the rank of independent variables in a mathematical sense. This implies that they may occur in nature in various kinds of combinations or constellations. These variables are commonly designated as "soil-forming factors."

Equation (*1*) as such is of limited pedologic use. When it is resolved into its components, however, the resulting individual functions of soil-forming factors are valuable guides in the study of soil genesis. With considerable justification they may be termed the five canonical functions of pedology. Briefly, the functions are as follows:

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Time functions, or chronofunctions:

$$s = f(t)_{cl, o, r, p, \ldots}$$

Soil properties are related to time under conditions of constancy of cl, o, r, p.
Parent material functions or lithofunctions:

$$s = f(p)_{cl, o, r, t, \ldots}$$

Soil properties are related to parent material under conditions of constancy of cl, o, r, t.
Topography functions or topofunctions:

$$s = f(r)_{cl, o, p, t, \ldots}$$

Soil properties are correlated with topographic features when cl, o, p, t are constant.
Climatic functions or climofunctions:

$$s = f(cl)_{o, r, p, t, \ldots}$$

Soil properties are expressed in terms of climatic variables when o, r, p, t are constant.
Organism functions or biofunctions:

$$s = f(o)_{cl, r, p, t, \ldots}$$

Dependency of soil properties on organic species. These functions deal with relationships between soil properties and organisms when cl, r, p, and t are constant.

The soil-forming factors cl, o, r, p, are multiple factors and yield groups of functions.

CRITERIA FOR APPROXMIATIONS

The precise evaluation of the five functions can be obtained under experimentally controlled conditions only. In the field it is extremely difficult to satisfy the required constancy of factors. Useful approximations to single-factor functions *within a given area* may be obtained when the amount of change of a soil property (s) conditioned by one factor greatly exceeds the changes conditioned by all of the others. This may be the result of the following two possibilities:

1. One of the factors varies greatly, whereas the remaining ones vary, in comparison, but little.
2. Save for one function, the slopes of the others are nearly 0. In other words, some factors may vary considerably, yet be of relatively little importance in determining differences in soil properties.

If in a given area a soil property s varies from s_a to s_b, and if the soil-forming factors F_1, F_2, F_3, F_4, F_5 vary from c to d, e to f, g to h, i to j, and k to l, respectively, we may write

$$s_b - s_a = \int_c^d \left(\frac{\partial s}{\partial F_1}\right) dF_1 + \int_e^f \left(\frac{\partial s}{\partial F_2}\right) dF_2 + \int_g^h \left(\frac{\partial s}{\partial F_5}\right) dF_3$$
$$+ \int_i^j \left(\frac{\partial s}{\partial F_4}\right) dF_4 + \int_k^l \left(\frac{\partial s}{\partial F_5}\right) dF_5 \tag{2}$$

Should the definite integrals of the factors F_2, F_3, F_4, F_5 be small in comparison with the definite integral of F_1, we may say that $s_b - s_a$ is mainly conditioned by F_1. The factor F_1 is dominant, all others are subdominant. Such conditions frequently obtain under field conditions. Equation (2) is a precise and concise formulation of the conditions enumerated above under 1 and 2. It serves as a guiding principle for the evaluation of functions in the field.

SOIL SEQUENCES

Soils have many properties. Since each property is assumed to obey equation (1), a large number of equations of the following type are obtained:

$$s_1 = f_1(cl, o, r, p, t, \ldots)$$
$$s_2 = f_2(cl, o, r, p, t, \ldots)$$
$$s_3 = f_3(cl, o, r, p, t, \ldots)$$
$$s_n = f_n(cl, o, r, p, t, \ldots)$$

All properties (s_1, s_2, s_3, etc.) taken together constitute a collection, assemblage, or ensemble of properties which is the soil. If we designate the ensemble of s values with the symbol $E_{(s)}$ we may write

$$\text{Soil} = E_{(s)} = f(cl, o, r, p, t, \ldots) \tag{3}$$

Just as each individual s property is a function of soil-forming factors, so is the entire ensemble dependent on cl, o, r, p, and t. In practice, the variations of the ensemble are recognized as soil types and soil series. In accordance with the five pedologic functions, the ensembles, that is, soil types and soil series, may be arranged in five sequences; namely, chrono-, litho-, topo-, climo-, and bio-sequences.

CHRONOSEQUENCES

In accordance with the relationship

$$\text{Soil} = E_{(s)} = f(\text{time})_{cl, o, r, p, \ldots}$$

Soil series and types may be placed in time or maturity sequences. A well-known example is furnished by Shaw's San Joaquin family (9). It comprises the following sequence of soil series:

(Tujunga), Hanford, Greenfield, Ramona, Placentia, (San Joaquin).

There is some controversy as to whether the San Joaquin series and possibly the Tujunga series are members of the sequence. The entire sequence is inferred from physiographic relationships and profile features.

Segments of the San Joaquin chronosequence occur in the Riverside Area, California (7), for which the conditioning factors may be indicated as follows:

cl = annual rainfull 10–20 inches, annual temperature 61–63°F.; moist mild winters and hot dry summers. In the vicinity of the City of Riverside (rainfall 11 inches) five of the series occur adjacent to one another.

o = grasses and shrubs; land now cultivated.

r = gently sloping alluvial fans and terraces; no ground-water influences.

p = coarse-textured alluvium derived from granitic rock sources.

t = Pleistocene and Post-Pleistocene to recent.

TABLE 1

Soil characteristics of the San Joaquin chronosequence in Riverside Area, California

SERIES	COLOR		TEXTURE		pH RANGE IN PROFILE (NO. CaCO₃ PRESENT)
	Surface	Subsoil	Surface	Subsoil (B horizon)	
Tujunga...............	gray	gray	sandy	sandy	7.2
Hanford	brown	light brown	sandy loam	sandy loam	7.0–7.4
Greenfield.............	brown	brown	sandy loam	sandy loam having more clay	7.4
Ramona	brown	reddish brown	sandy loam	sandy clay loam	7.2–8.0
Placentia	reddish brown	reddish	sandy loam	clay loam or clay	7.0–8.2
San Joaquin	not present in Riverside Area				
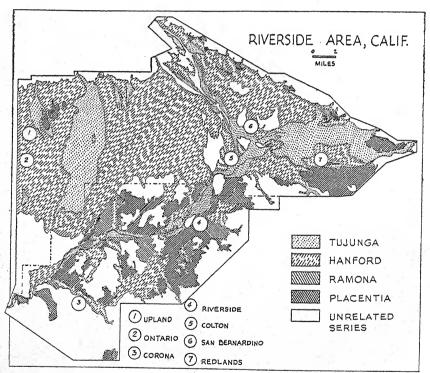
FIG. 1. GEOGRAPHIC SETTING OF A CHRONOSEQUENCE (SHAW'S SAN JOAQUIN FAMILY) IN THE RIVERSIDE AREA, CALIFORNIA

Numbers in circles refer to towns. The Greenfield series has not been separated in this area; it is included with the Hanford series.

A brief characterization of the various series is given in table 1. The degree of development of the B horizon is the main criterion used in establishing the relative age and therefore the order of the series within the sequence. The geographic setting is shown in figure 1.

LITHOSEQUENCES

According to the relationship

$$\text{Soil} = E_{(s)} = f(\text{parent material})_{cl,\ o,\ r,\ t,\ \ldots}$$

it should be possible to group soil types and series in relation to parent material. Two examples may serve as illustrations.
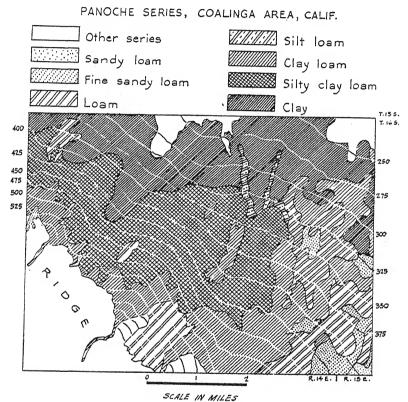
FIG. 2. LITHOSEQUENCE OF SOIL TYPES OF THE PANOCHE SERIES, COALINGA AREA, CALIFORNIA

White lines are 25-foot contour intervals.

In the Coalinga Area, California, the region between Monocline Ridge and Fresno Slough is occupied by gently sloping colluvial fans consisting of outwash from the softly consolidated calcareous sandstones and shales of the Coast Range Mountains. In recent years a large body of Panoche series, having wide textural range, has been mapped in the fan area.[2] There are nine textural groups

[2] Harradine, F. F. Soils of western Fresno County, California. 1943. [In manuscript.]

which, within themselves, have uniform textural profiles.   The soils are brownish gray or grayish brown, calcareous throughout, deep, and friable.   They become sticky when wet.   The subsoils are slightly browner and may show stratification. The soil-forming factors of the area shown in figure 2 are as follows:

cl = annual rainfall 6–8 inches, annual temperature 62–64°F.; hot dry summers, mild winters.

o = grasses and shrubs.

r = gently sloping fan; no ground-water influences.

p = alluvial fans varying in texture from sands to clays.

t = unknown, but presumably of the same order of magnitude for all types within the series.

The slope of the fan varies slightly, being about 2 per cent at the upper portion and 1 per cent at the lower.   This variation is characteristic for all Panoche soil types shown in figure 2.   According to field observations, it does not appreciably influence profile features.

When all facts are taken into consideration, it is apparent that the type differentiations within the Panoche series are conditioned by parent material.   There exists then a lithosequence of Panoche types: sandy loam, fine sandy loam; loam, silt loam, clay loam, silty clay loam, silty clay, clay.

This sequence is nearly continuous in character.   One might, for example, plot the nitrogen content of these soils as a function of their moisture equivalents, the latter being convenient quantitative expressions of the textures of the parent materials.

The great range in textural variations within the Panoche series is likely to be associated with significant differences in the mineralogical and chemical composition of the parent materials.   If soil series were monotypes, the foregoing soil type sequence would become a lithosequence of soil series.

The second illustration of a lithosequence embraces the following four upland soil series that were mapped within the San Mateo Soil Conservation District, California (2):

Colma series, derived from semiconsolidated marine and coastal plain sediments and sandstones.

Hugo series, derived from sandstone and shale.

Sweeney series, derived from basic igneous rock (basaltic).

Sheridan series, derived from acid igneous rock (quartz diorite).

As shown by Barshad[3] the Colma, Sweeney, and Sheridan series are prairie soils insofar as color, organic matter, structure, and reaction are concerned. Other properties, especially chemical composition and nature of clay minerals, vary widely among the three series studied by Barshad.   The soil-forming factors of the region (fig. 3) are as follows:

[3] Barshad, I.   A pedologic study of California prairie soils.   1944.   [Unpublished thesis, University of California.]

cl = annual rainfall 25–45 inches, annual temperature 56°F. (San Francisco); mild wet
      winters and dry, cool, but foggy summers.

o = grasses and chaparral.

r = hilly to mountainous, the dominating slopes exceeding 10 per cent; well drained.

p = igneous and sedimentary rocks.

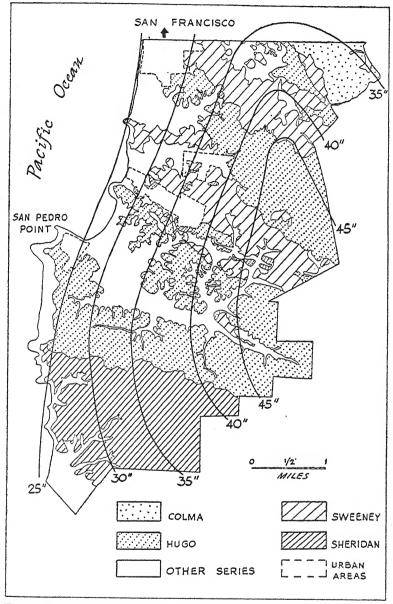t = similar for all four series, as judged by physiographic relationships.

FIG. 3. LITHOSEQUENCE OF SOILS IN THE SAN MATEO AREA, CALIFORNIA
Black lines indicate annual precipitation.

Within each of the four series, rainfall and slope vary considerably. Field inspection and reaction tests do not disclose a discernible climatic moisture effect within the range of variability of each series. We have here a case where a considerable latitude in rainfall is not accompanied by corresponding variations in soil properties. With reference to equation (2) the definite integral

$$\int_{cl_1}^{cl_2} \left(\frac{\partial s}{\partial cl} \right) dcl \qquad (cl = \text{climate})$$

apparently is of relatively small magnitude and may be neglected. More detailed and systematic field studies in relation to rainfall might reveal small climatic moisture effects within the series as now defined.

As indicated, slope is extremely variable within each series. As it is possible to compare representatives of all four series on equal slopes and thus fulfill the requirements of equal slopes, we may form the following lithosequence of series: Colma, Hugo, Sweeney, Sheridan. The order of the series within the sequence is based, approximately, on the increasing hardness of the parent material, which in turn bears some relationship to the depth of the soil.

In general, the specific order of series chosen within a lithosequence is guided by the soil properties to be emphasized. According to Barshad, clay formation in these soils is conditioned largely by the mica and augite content of the rock. One might therefore prefer to arrange the series according to the content of the clay-forming minerals. For other interpretive purposes, the lime content of the parent material, or its texture, might be chosen.

The soil families of Brown and Thorp (3) are lithosequences, restricted to closely allied parent materials such as lithologic variations within a glacial drift.

TOPOSEQUENCES

Toposequences are related to the dependency

$$\text{Soil} = E_{(s)} = f(r)_{cl, \, o, \, p, \, t, \, \ldots}$$

The soil-forming factor topography is of a complex kind, for it includes, in additio to degree of slope, shape of slope (convexity and concavity), length of slope, and possibly exposure, certain hydrologic features commonly referred to as drainage.

In setting up equation (1) it was assumed that for a given set of o, p, and t, the air climate (cl) and the topography (r) govern the soil climate (cl'), in particular the moisture regime of the soil. This is true only in the absence of a free or perched water table. From the viewpoint of soil formation, it is important to distinguish between primary and secondary or pedologic water tables.

Figure 4 schematically depicts a segment of a landscape. In the trough the presence or absence of a free or perched water table mainly depends on the permeability of the land surface, degree of slope, length of slope, and climate. The presence of a water table may thus be considered a dependent variable, being favored by certain constellations of cl, r, and p. If, however, such a dependency already exists at the soil-formation time 0, it is more convenient to treat the

water table as an independent variable or soil-forming factor. Such water tables (perched or ground water) may be thought of as primary water tables. Water tables conditioned by geologic and physiographic relationships, such as streams, lakes, and ponds, are primary water tables.

In arid regions, the presence or absence of a water table often is a function of time of soil formation. Consider figure 4 to represent a land surface, at 0 time, consisting of very porous, sandy alluvial material. Under moderate rainfall, no free water accumulates in the trough. As soil genesis proceeds, the material tends to become less permeable, because of clay formation and horizon development. In due time a temporary or even permanent water table may appear (e.g., Redding and Alamo series).

The situation may be analyzed from two different points of view. First, we may consider the water table a truly dependent variable, being conditioned for a given combination of cl, o, r, p by the time t. Such a water table, perched or any
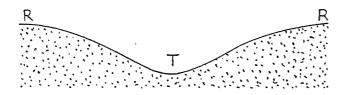
FIG. 4. SEGMENT OF LANDSCAPE WHICH MAY HAVE PRIMARY OR SECONDARY WATER TABLES

other type, is designated as a secondary or pedologic water table. Accordingly, in figure 4, the soils at T and R constitute a simple topography sequence, the factors cl, o, p, t being identical. The second point of view would consider the secondary water table an independent soil-forming factor, that is, treat it as a primary water table. Conceivably at some arbitrary time when the water table has appeared, a new cycle of soil formation would begin in the trough, while on the ridge the processes would continue uninterruptedly. By definition, the soil in the trough at the beginning of the new cycle would become parent material. At some later stage the soils at R and the new soil at T would no longer constitute a simple toposequence, but rather a complexity differing in $r, p,$ and t. If we place emphasis on soil genesis, the first alternative, which recognizes a pedologic water table, appears simpler and more straightforward.

Some of the possible combinations of slopes of land and positions of primary free or perched water tables are shown in figure 5. To a considerable extent, slope (i) and water table (w) may be treated as independent variables and we may resolve the function

$$s = f(r)_{cl, o, p, t, \ldots}$$

into

$$s = f(i, w)_{cl, o, p, t, \ldots}$$

where i is the slope and w the plumb distance from the surface of the soil to the water table. For a given combination of cl, o, p, t, certain aspects of soils, for example, soil depth and erosion, are primarily conditioned by i (clinofunctions); whereas others, such as degree of oxidation and mottling, are more nearly functions of w (hydrofunctions).
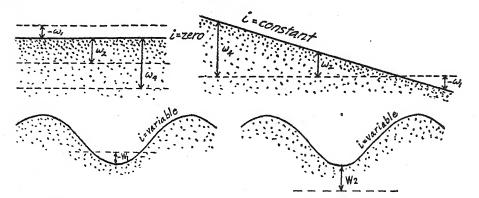
FIG. 5. VARIOUS COMBINATIONS OF SLOPES (i) AND FREE WATER TABLES (w)
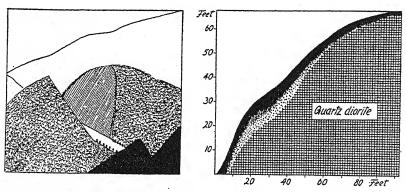
FIG. 6. A SLOPE SEQUENCE (CLINOSEQUENCE) WITHIN THE SHERIDAN SERIES

Left: sketch showing deep road cuts through chaparral-covered hills of "soft" quartz diorite. Right: exposed soil mantle illustrating depth of soil in relation to slope.

Substituting soil series or types for the single property s, we obtain toposequences which may be divided into clinosequences, hydrosequences, and possibly others. Bushnell's (5) profiles VI and IV are members of slope sequences, whereas others (II, I, VII, VIII, IX) constitute hydrosequences. Bushnell's catenas are combinations of clinosequences and hydrosequences. Both i and w vary simultaneously.

Good illustrations of *clinosequences* are found in the aforementioned Sheridan series. The left half of figure 6 shows the general topographic features, whereas the right half illustrates the relationship between depth of soil and slope. This

differentiation in depth and associated soil properties is brought about by variations in soil climate and soil creep, both being functions of slope.   There is no
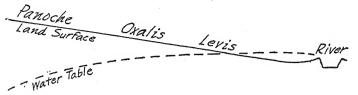
FIG. 7. SURFACE CONFIGURATION AND WATER TABLE OF PANOCHE HYDROSEQUENCE
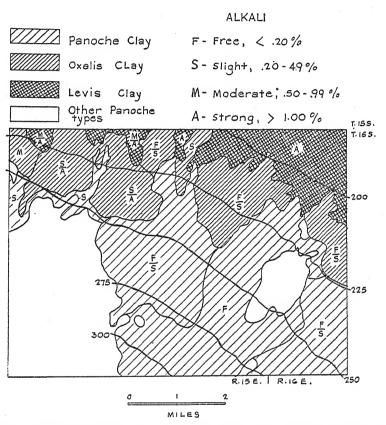
FIG. 8. HYDROSEQUENCE OF SOILS ON THE LOWER END OF THE "PANOCHE FAN," COALINGA AREA, CALIFORNIA

Note constancy of slope, and alkali accumulation at the lower end of the fan.   Single letter indicates alkali condition throughout the profile.   Quotient of letters denotes salinity in surface (numerator) and in subsoil (denominator).

free water table; in other words, $\dfrac{\partial s}{\partial w} = o$.   The sequence, as mapped, is Sheridan sandy loam, *shallow phase*; Sheridan sandy loam, *deep phase*.

An example of a *hydrosequence* is given by the series sequence Panoche clay, Oxalis clay, Levis clay. These three series occur in the Coalinga Area, California, on portions of alluvial fans having nearly constant slope. The soils are derived from calcareous and gypsiferous sandstones and shales. All series are calcareous throughout and contain variable amounts of gypsum. During the rainy season, overflow water and ground water maintain varying degrees of wetness on the lower ends of the fans. These hydrologic conditions have brought about a differentiation of the uniform Panoche fan material into the Oxalis and Levis seres (table 2). In winter, the water table is probably of the type shown

TABLE 2

Soil characteristics of the hydrosequence shown in figure 9

(All soils contain lime and gypsum throughout the profile)

SOIL TYPE	Panoche clay	Oxalis clay	Levis clay
Slope, *per cent*	0.8	0.8	0.8
Depth to highest water table, *feet*	>20	2–5	0 or negative
Color of surface soil	light brownish gray	dark brownish gray	brownish gray
Color of lower subsoil	brown	grayish brown, slight mottling	light brown
Development of B horizon	none	high concentration of lime and gypsum	slight vertical cracking
Alkali	none to slight	slight to moderate	very high

in figure 7. There is no water table in summertime. The areal extent of the sequence and the distribution of alkali are shown in figure 8. The soil-forming factors climate, vegetation, parent material, and time of this area are identical with those of the Panoche lithosequence.

CLIMOSEQUENCES

In the relationship

$$\text{Soil} = E_{(s)} = f(cl)_{o,\ r,\ p,\ t,\ \ldots}$$

climate (*cl*) denotes a multiple soil-forming factor. It may be resolved into moisture (*m*) and temperature (*T*) components, as follows:

$$\text{Soil} = E_{(s)} = f(m,\ T)_{o,\ r,\ p,\ t,\ \ldots}$$

By analogy one may arrange soil types and series in climosequences, hygrosequences, thermosequences, and possibly others.

Because of its wide variations in climate, California offers an attractive field for the search of climosequences. However, a survey of the existing soil series in the state discloses certain difficulties. In the past the parent materials were

defined rather loosely, such as sedimentary rocks and acid igneous rocks. These groupings are too broad to establish well-defined climosequences of soils. Furthermore, many of the soil series were rather "elastically" defined as regards climatically controlled soil properties such as organic matter content and lime

TABLE 3
Tentative climosequences in California
(Within each sequence the time factor is considered comparable)

PARENT MATERIAL FACTOR	TOPOGRAPHY FACTOR	BIOTIC FACTOR	HYGROSEQUENCES		
			Arid	Transition	Humid
Acid igneous rocks	variable	grass, forest	Vista ⟶ Holland		
Acid igneous rocks	variable	grass, forest	Fallbrook ⟶ Sierra		
Basic igneous rocks	variable	grass, shrub	Las Posas → Sobrante → Sweeney		
Soft sedimentary rocks, noncalcareous........	variable	grass	Altamont ⟶ Los Osos → Colma (lime-free phase)		
Consolidated sedimentary rocks, noncalcareous..	variable	grass, forest	Vallecitos ⟶ Hugo		
Alluvium, acid igneous source......	gentle slopes	grass, shrubs	Mohave → Merriam (?)		
Alluvium, acid igneous source, wind-modified....	undulating	grass, shrubs	Coachella → Delhi		
Alluvium sedimentary	gentle slopes	grass, forest	Panoche ⟶ Sorrento; Yolo ⟶ Soquel		
Mixed alluvium, wind-modified....	undulating	grass	Rositas ⟶ Oakley ⟶ Marina		

content. In other words, many series are extremely variable. A tentative list of California climosequences, mainly hydrosequences, is given in table 3.

BIOSEQUENCES

In the equation

$$\text{Soil} = E_{(s)} = f(o)_{cl,\ r,\ p,\ t,\ \ldots}$$

o denotes organic species and their frequencies. In nature, biosequences are difficult to evaluate. In comparing different biotic factors, such as forest and prairie, we must be reasonably sure that they are not themselves functions of the

soil-forming factors cl, p, r, and t.   In California, the relationship between soil series and biotic factors has not yet been sufficiently explored to establish biosequences.   In Bushnell's key to soils of Indiana (5), are listed a number of series that vary in vegetation and that may be placed in biosequences.   An illustration is given in table 4.   It contains four biosequences (or "florsequences," according to Bushnell), each being derived from the same parent material but each having different topographic positions.   Climatic and time factors presumably are the same for all series.   The four biosequences are arranged from left to right   The arrangements from top to bottom within each vegetational group constitute toposequences (catenas).

TABLE 4

Examples of biosequences in Indiana

From Bushnell (5)

PARENT MATERIAL	TOPOGRAPHY		BIOSEQUENCES		
	Slope (i)	Average Depth to water table (w)	Prairie	Transition	Forest
	per cent	*feet*			
Till of variable lithologic composition and medium texture, high in lime	4–15	>3	Parr ⟶ Octagon ⟶ Miami		
	1– 2	3 to 1	Odell ⟶ Otterbein ⟶ Crosby		
	0– 1	0 to −3*	Drummer ⟶ Drummer ⟶ Brookston		
	0– 1	> −3	Clyde ⟶ Clyde ⟶ Kokomo		

* The minus sign indicates that the surface of the soil is under water.

In connection with the biotic factor, the following question is frequently asked: What is meant by "constant vegetation" for a group of soils belonging to a catena or to any other soil sequence?   According to preceding discussions, the relationships

$$\text{Soil} = E_{(s)} = f_t(t)_{cl,\ o,\ r,\ p,\ \dots}$$
$$\text{Soil} = E_{(s)} = f_p(p)_{cl,\ o,\ r,\ t,\ \dots}$$
$$\text{Soil} = E_{(s)} = f_r(r)_{cl,\ o,\ r,\ t,\ \dots}$$
$$\text{Soil} = E_{(s)} = f_{cl}(cl)_{o,\ r,\ p,\ t,\ \dots}$$

imply constancy of the biotic factor (o) within each sequence.   Yet, as is well known, vegetation may vary within a sequence.   In Indiana, for example, the Miami catena is characterized by an oak-hickory forest, but the distribution of the various plant species varies with slope and hydrologic conditions.   More striking variations are encountered in arid regions.   Within a hydrosequence, grass may be abundant on the well-drained areas, whereas no vegetation at all grows on the depressional salt flats.   In these and many other sequences vegetation is certainly not constant.   Growth and distribution of species are clearly variable, being conditioned by cl, r, p, and t.   On the other hand, seeds of all the species of a sequence probably have a chance to fall on all soils of the sequence. In this sense, all soils of the sequence have the same biotic factor.   Placing em-

phasis on potential vegetation (seeds) rather than on actual growth, which is always a dependent variable, we may define the biotic factor of a sequence as the sum total of the species associated with it. On these grounds, we are justified in considering the biotic factor of a sequence a constant, the frequency effect being negligible.

RELATION TO BUSHNELL'S SYSTEM

A certain connection exists between the author's soil sequences and Bushnell's multiple catenas (4), although the two approaches were developed independently of each other. Interestingly enough, the Indiana system grew out of Bushnell's field experience by the process of induction, whereas the system of sequences was derived by the process of deduction from the generalized equation of soil forming
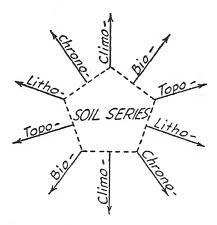
FIG. 9. INTERLACING OF SOIL SERIES

Each soil series belongs to five sequences and in general is genetically related to ten other series.

factors. The fact that the two systems closely harmonize speaks well for their soundness.

According to the writer's viewpoint, every homogeneous soil type or series belongs, theoretically, to each of the five canonical functions or sequences. For example, the Panoche clay appears as an initial member of a climosequence (table 3), of a toposequence (table 2), and of a chronosequence (not yet fully established). Also, it is an end member of a lithosequence (fig. 2). Its status in a biosequence is as yet uncertain. The author considers the five sequences of equal categorical rank. Since each soil series is a member of five functions, it is thus pedogenetically connected with ten other series, unless it happens to be an initial or end member of a sequence. This relationship is diagrammatically illustrated in figure 9.

To portray all five sequences simultaneously would require a five-dimensional arrangement. In practice, so-called keys may be constructed in which the five soil-forming factors appear in a complicated nest of blocks. Within each block

there is a lattice of pigeonholes containing the soil series names. In Bushnell's Indiana key (5) topography and parent material determine the broad framework. In the author's unpublished California key, which contains over 300 soil series, climate and parent material govern the rows and columns, as indicated in table 3. Unlike the Indiana key, the California key does not contain profile descriptions ("major profile") as essential parts of the headings. According to equation (1) the soil profile is a dependent variable and is assigned, therefore, to the pigeonholes exclusively. The headlines are reserved for the independent variables, the soil-forming factors.

As an additional approach, Bushnell (4) suggested giving the toposequence (catenas) preferred categorical rank. Instead of having five coordinate sequences (chrono-, litho-, topo-, climo-, and biosequences) there would be four sequences of catenas: chronoacatenas, lithocatenas (byndels), climocatenas, and biocatenas (florcatenas).

SIGNIFICANCE OF SEQUENCES

Soil sequences may be considered a classification of soil series and types in accordance with the five canonical functions of pedology. This classification contains but one postulate: soils vary in a continuous manner as formulated by the soil-forming factor equation (1). The classification is truly pedologic, for it borrows no basic concepts from other sciences. True enough, mathematics is involved, but merely for clarity of thought and convenience of expression. The classification is genetic. The soil profile, as embodied in the concept of a soil series, is related to its origin. The inclusion of the coordinates cl, o, r, and p gives the scheme geographic significance.

From the system of five sequences one may "carve out" any number of convenient soil groupings. All zonal, intrazonal, and azonal soils, as well as families (Brown and Thorp's), catenas, fascs may be considered more or less arbitrary delineations within the five pedologic sequences.

As far as available records indicate, it appears that Dokuchaev came closest to establishing equation (1). It is not clear from Russian writings (1, 8) whether his formula was an actual equation in the mathematical sense, or merely a shorthand statement on the role of soil-forming factors. Neither Dokuchaev nor his pupils seem to have derived the five canonical functions.

SUMMARY
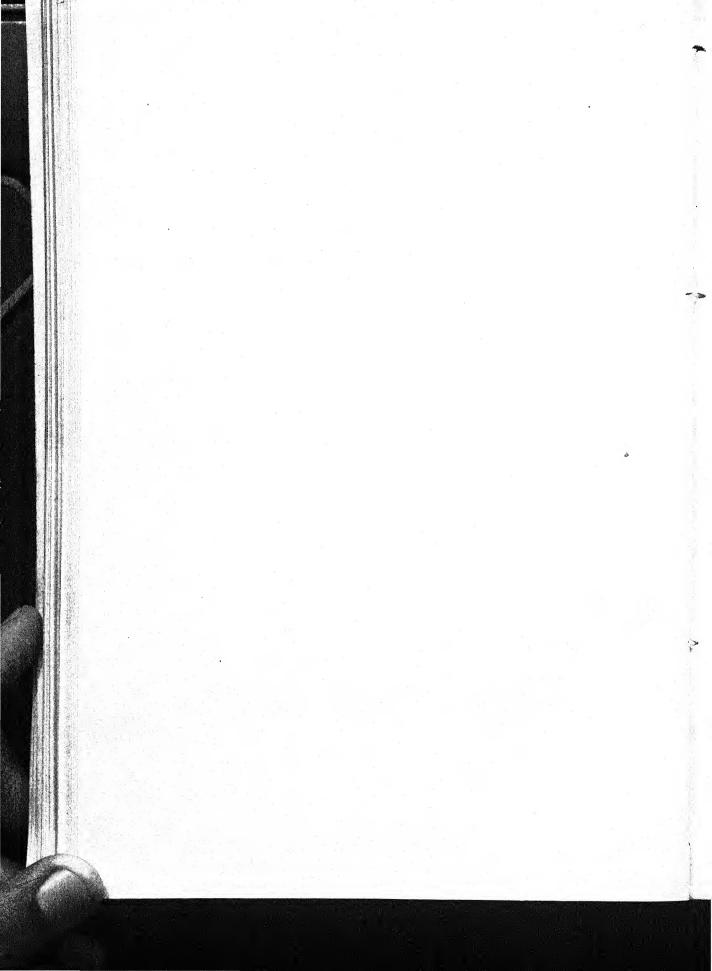
On the basis of the generalized equation of soil-forming factors, five groups of pedologic functions are recognized. Criteria are given for evaluating in a given area the dominant and subdominant soil-forming factors.

Soil series and types are arranged in five sequences: chronosequences, lithosequences, toposequences, climosequences, and biosequences. Their relationships to Bushnell's multiple catenas and Thorp's families are brought out.

The genetic classification of soil series constitutes a five-dimensional network of series. Each soil series is linked, in principle, to ten other series.

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EFFECTS OF ORGANIC RESIDUES AND NITROGEN FERTILIZERS ON A SEMIARID SOIL[1]

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Various studies (2, 3, 6, 9, 13, 18, 19) indicate that prolonged periods of dry-land farming of semiarid soils result generally in a loss of soil organic matter. There is fairly good agreement among investigators (12, 15, 17, 20) that this loss can be minimized or overcome by applications of organic residues. It has been shown (1, 8, 16, 21, 23), however, that crops immediately following additions of strawy residues to the soil suffer from lack of available nitrogen. Some investigators (7, 10, 14, 18) maintain that inadequate supplies of available nitrogen in the soil are reflected in a reduced protein content of wheat grown on such soil, whereas others (5, 10, 21) contend that climatic factors rather than available nitrogen are the controlling principles.

The widespread use of tractors in the semiarid area in Washington has greatly reduced the amount of manure available. The legumes that are commonly used for green manures do not produce enough tonnage on the limited supply of available moisture to warrant their use. If a suitable legume were grown for green manure, it is likely that the supplies of available moisture and nitrogen would be unbalanced and result in subsequent burning effect on crops. Straw usually is available in large quantities, and on many farms it is applied to the land by a spreader attachment on the combine. The utilization of this natural crop residue with suitable additions of commercial nitrogen offers a possibility of maintaining the supply of soil organic matter and nitrogen in dry-land farming. This paper deals with a field experiment designed to determine the effect of wheat straw, manure, and nitrogen fertilizers on the organic matter and nitrogen supply of a semiarid soil at Lind, Washington, and on the yield and nitrogen content of wheat produced on this soil over a period of 18 years.

EXPERIMENTAL CONDITIONS AND METHODS

Climate

The climate at the Adams Branch Experiment Station, Lind, Washington, the site of the field experiment, is moderate. During the period 1920–1940 the month of July had the highest mean temperature (72.2°F.), and January the

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TABLE 1

Precipitation and yield data as compared with the average for the crop years 1918 to 1940 inclusive at the Adams Branch Experiment Station

YEAR	PRECIPITATION					YIELD OF BAART WHEAT	PER-CENT-AGE OF MEAN YIELD	REMARKS
	Crop year*	Fallow year†	Total 2 years‡	Percent of 2-year mean	In June			
	in.	in.	in.		in.	bu.		
1917	7.60	....	.....	...	....	....	...	
1918	6.64	3.29	9.93	74	0.10	6.8	54	
1919	8.10	4.68	12.78	95	0.00	14.1	111	High winter absorption
1920	6.56	6.16	12.72	95	0.60	10.1	79	
1921	7.01	2.39	9.40	70	0.20	11.7	92	
1922	6.97	5.33	12.30	92	0.58	6.3	50	Late seeding, cold spring and hot summer
1923	10.90	5.16	16.06	119	3.69	22.9	180	Early spring and June rain
1924	6.62	4.46	11.08	82	0.08	10.4	82	Dry spring and hot summer, drying winds
1925	8.32	5.48	13.80	103	0.23	14.9	117	Early spring, good rains in April and May
1926	6.65	5.56	12.21	91	0.64	15.4	121	Early spring, warm April and normal June
1927	12.65	3.36	16.01	119	0.96	15.7	124	
1928	10.83	6.80	17.63	131	0.56	16.3	128	
1929	5.77	8.83	14.60	109	1.35	11.1	87	Cold April, reserve moisture
1930	4.80	3.73	8.53	63	0.49	5.6	44	
1931	6.91	2.58	9.49	71	1.35	4.1	32	
1932	9.78	4.80	14.58	108	0.03	12.7	100	
1933	8.39	7.65	16.04	119	0.37	19.2	151	Early spring, warm March, cool May and June
1934	9.79	5.37	15.16	113	0.80	13.9	109	
1935	7.48	7.39	14.87	111	0.19	13.2	104	
1936	8.09	6.05	14.14	105	1.73	12.7	100	
1937	8.93	5.09	14.02	104	2.22	13.2	104	
1938	11.89	4.14	16.03	119	2.08	16.5	130	
1939	5.32	9.08	14.40	107	0.19	12.1	95	Weed infestation reduced yield
1940	13.01	4.29	17.30	129	0.40	15.8	123	
Mean..	8.29	5.29	13.40	...	0.82	12.8	...	

* Total precipitation for the periods of September 1 to August 31 in the year the crop is harvested.

† The precipitation for months April to September, inclusive is excluded from the total rainfall in the summer-fallow year.

‡ The amounts in this column represent 2 years' accumulation for the production of the single crop under the summer-fallow system practiced in the Lind area. The rainfall for the period of April to September inclusive for the summer-fallow year is excluded.

lowest (27.8°F.). The mean annual temperature was 49.7°F., the average daily maximum 61.6°F., and the average daily minimum 37.9°F. The growing season averaged 146 days.

Marked variations in rainfall and crop yields occur, as may be noted in table 1. Although the mean annual precipitation for the crop years of 1920 to 1940 was 8.51 inches, that for the crop year of 1939–40 was 13.01 inches, and that for the crop year of 1929–30 only 4.8 inches. Forty per cent of the total precipitation normally falls from November 1 to February 28, and 31 per cent from March 1 to June 30. Most of the rains that occur during April, May, July, August, and September are too light to penetrate into the root zone and, therefore, contribute little to crop growth. Some effective rains occur in June and occasionally in May. Since a crop under the fallow system benefits from the accumulated moisture of two years, a tabulation of the rainfall, excluding that for the months of ineffective rainfall during the fallow year is indicated in table 1, which is helpful in accounting for the variations in crop yields.

Soil and plot arrangement

The soil is Ritzville very fine sandy loam, which is widely distributed in central Washington. It contains approximately 1 per cent of organic matter,

TABLE 2
Arrangement and treatments of the field plots

PLOT NUMBER	TREATMENTS	AMOUNTS PER ACRE
		lbs.
603-1812	Check (binder stubble returned)	....
604-1813	Wheat straw	1,600
605-1814	Wheat straw	3,200
606-1815	Wheat straw	800
607-1816	Ammonium sulfate	50
608-1817	Check (binder stubble returned)	....
609-1818	Wheat straw	800
	Ammonium sulfate	50
610-1819	Wheat straw	1,600
	Ammonium sulfate	100
611-1820	Ammonium sulfate	100
612-1821	Manure	7,000
613-1822	Check (binder stubble returned)	....

is light grayish brown, and is underlain by a lighter colored subsoil. A calcium carbonate layer is ordinarily present at depths of 3 to 6 feet. The soil is floury and subject to blowing when improper tillage methods are followed. In fact, the land on which the field plots were established had been abandoned as "blow land" when taken over by the state for an experiment station.

Two series of plots, the 600 and 1800 series situated about $\frac{1}{2}$ mile apart on the farm, were established in 1922. Both series have a southern exposure with a gentle slope, and to all appearances are comparable. The plots are rectangular, 132 feet long and 16.5 feet wide, constituting an area of $\frac{1}{20}$ acre, and have 5-foot alleys between them. The arrangement and treatments for both series of plots are given in table 2.

The straw applied to the plots represented field run lots; that produced on the individual plots was not returned to these plots. On the basis of previous yields the 1600-pound application of straw was intended to represent the average amount of straw produced in years when grain yields are considerably above average. The 7000-pound application of manure was intended to supply an amount of nitrogen equivalent to that in 1600 pounds of straw supplemented with 100 pounds of ammonium sulfate. As the moisture content of the manure used was generally low, it is likely that the manure contributed more nitrogen and considerably more dry matter than the 1600 pounds of straw and 100 pounds of ammonium sulfate.

The treatments originally were to be applied in fall, the plots plowed in early spring, summer-fallowed, and sown to fall wheat of the Turkey variety. Since 1936 the straw was applied in fall, however, and the nitrogen fertilizer and manure in the spring previous to plowing. Much of the time, conditions proved to be unfavorable for fall wheat, and therefore, spring wheat of the Baart variety was grown in 1925, 1929, 1931, 1932, 1933, and annually since 1936 in order to obtain satisfactory yields. All plots were tilled in the same manner, series 600 being cropped during odd-numbered years and series 1800 during even-numbered years.

Methods of harvesting and sampling

The entire plots were harvested to determine the yields of grain and straw.

The soil samples taken in 1922 for nitrogen and carbon determinations were composites from nine borings made to a depth of 6 inches at points systematically distributed over each plot. The samples for 1940 were taken from six borings to a depth of 6 inches systematically placed.

Soil samples for moisture and nitrate-nitrogen determinations were taken annually early in the spring at six locations on each plot and composited. The sampling was done in 1-foot sections to the depth of moisture penetration, usually 4 to 6 feet.

Methods of analysis

The A. O. A. C. methods (4) were used for the determination of nitrogen in the grain and straw, and of nitrogen and carbon in the soil, all analyses being based on oven-dry weights (105°C.). The carbon and nitrogen in soil samples taken in 1922 were determined on a single composite sample from each plot, and on three separate samples from each plot for the samplings in 1940. The results of the latter were averaged. Large portions of soil were taken for analysis, and reagents of low normality were used to increase the accuracy of the determinations.

EXPERIMENTAL RESULTS

Yields of grain

Any soil management system that builds up soil organic matter, or contributes favorably to its maintenance, should increase or at least maintain the yield

of grain.   The wheat yields for the experimental plots as affected by the various soil treatments are summarized in table 3.

Marked variations in yield occurred from year to year on the same plot as well as on different plots in relation to those of the check plots.   For example, plot 611–1820, receiving 100 pounds of ammonium sulfate per acre, produced the highest yield in 1927, whereas in 1939 it was nearly the lowest in yield. Other plots varied similarly.   Since the tillage methods and harvesting procedures were identical for all plots, the factors which most likely affected the yields are available moisture, distribution of rainfall, soil conditions, and possibly

TABLE 3

Annual and average grain yields per acre for the 600 and 1800 plot series from 1923 to 1940*

PLOTS	603-1812	604-1813	605-1814	606-1815	607-1816	608-1817	609-1818	610-1819	611-1820	612-1821	613-1822	AVER-AGE OF CHECKS
	bu.	bu.	bu.	bu.	bu.	bu.	bu.	bu.	bu.	bu.	bu.	bu.
1923	25.3	26.8	27.5	26.2	25.3	26.7	29.0	26.5	28.0	23.5	27.3	26.4
1924	15.7	14.7	14.5	14.0	13.3	14.8	14.5	14.8	14.8	16.3	15.7	15.4
1925	16.8	15.0	14.3	16.5	18.5	15.7	17.3	18.0	17.3	15.0	14.5	15.7
1926	13.7	16.8	16.2	15.8	14.8	16.8	16.0	16.2	15.8	16.7	13.0	14.5
1927	24.0	24.0	23.8	23.7	28.2	23.0	27.2	28.7	31.0	25.7	23.7	23.6
1928	28.8	28.2	28.5	26.5	30.7	28.7	32.2	28.2	29.5	30.7	26.2	27.9
1929	12.2	10.8	10.7	9.3	11.2	10.7	10.5	10.3	10.5	11.2	10.3	11.1
1930	7.2	5.7	6.3	6.8	6.0	7.7	8.0	7.5	7.0	7.2	7.8	7.6
1931	4.0	3.5	3.7	3.3	2.0	3.2	2.7	2.7	1.2	3.0	4.0	3.7
1932	11.3	11.7	11.0	10.7	12.2	11.3	12.7	12.7	11.2	12.0	10.8	11.1
1933	10.7	10.3	8.8	10.8	10.7	11.7	11.0	11.7	11.2	11.5	12.3	11.5
1934	20.0	19.3	19.0	18.3	15.8	20.9	15.2	15.2	15.7	19.4	18.5	19.8
1935	14.3	16.2	15.3	15.3	13.8	15.7	15.5	16.8	15.3	16.2	17.5	15.8
1936	12.2	12.6	11.2	11.6	10.2	13.2	13.4	12.2	10.2	12.4	12.9	12.8
1937	4.2	5.7	6.3	6.1	4.1	5.3	4.1	5.4	4.8	4.8	5.4	5.0
1938	19.3	21.1	20.8	18.3	15.0	18.3	18.8	16.2	16.0	17.8	16.8	18.1
1939	12.7	13.1	13.6	12.7	11.1	13.8	10.5	13.1	10.9	12.2	11.1	12.5
1940	15.3	17.1	15.3	15.3	16.2	15.5	18.0	17.3	16.2	18.9	15.0	15.3
Av.....	14.9	15.1	14.8	14.5	14.4	15.2	15.4	15.2	14.8	15.2	14.6	14.9

* Series 600 was cropped in odd-numbered years, and series 1800 in even-numbered years· See table 2 for treatments.

temperature relationships.   In years during which the moisture supply and growing conditions are such as to result in average or better than average yields under field practices, the yields on the plots receiving a substantial amount of ammonium sulfate alone or with straw would be expected to be larger and those on the plots receiving straw alone and smaller than the yields on the nonfertilized plots.   Conversely, during years when the moisture supply and growing conditions are less favorable, the plots receiving nitrogen might be expected to exhibit a decrease in yield.

Though a cursory inspection of the average plot yields presented in table 3 for the 18 years of the experiment shows no more than a trend in favor of certain soil treatments, a closer examination of the annual yields in relation to the data

in table 1, expressing soil moisture conditions by precipitation received as well as yields in percentage of the average yields at the station, provides a better perspective of the influence of the various soil treatments. For example, during the years 1925, 1926, 1927, 1928, and 1940 when the wheat yields at the Adams Branch Experiment Station were considerably above average, and after the soil treatments on the experimental plots had been repeated several times, the effect of the nitrogen fertilizers applied alone or with straw, or of the nitrogen applied in the form of manure, was generally manifested by increased yields. The applications of straw alone in various quantities produced no significant changes in yield. Since available soil moisture is one of the major limiting factors in wheat yields in the semiarid area represented by the station, it is reasonable to assume that any benefit that might be derived from applications of nitrogen to the soil would be most pronounced during years when soil moisture is most plentiful. This explanation does not hold, however, for 1933 and 1938 when the wheat yields at the station were considerably above average and the effect on yields resulting from any of the soil treatments was negligible. Apparently other factors, such as temperature relationships at critical periods of crop growth, counteracted the beneficial effect of favorable soil moisture conditions.

During the years 1924, 1929, 1930, and 1931 when the wheat yields and the supply of soil moisture, except that in 1929, were considerably below average at the station, the general effect of both nitrogen and straw applications was manifested by decreased yields, showing that stimulated vegetative growth in spring probably resulted in lack of moisture, which was the major limiting factor in yields.

Although no outstanding increases or decreases in wheat yields resulted from the various soil treatments during the experimental periods, the influence of nitrogen applied alone and as a supplement to straw, or as an ingredient of manure was generally shown by increased yields, when more than an average soil moisture supply favored yields considerably above average at the station. The effect of both nitrogen and straw additions was manifested generally by a reduction in yields when a limited supply of soil moisture resulted in yields considerably below average at the station.

Nitrogen content of the wheat

The grain and the straw were analyzed for nitrogen to determine the relative amounts of this element removed by the crops.

Figure 1 shows the average nitrogen content of the grain for 15 years. Although the nitrogen content fluctuated considerably from year to year, the differences for the average values are small. The trends indicated for the two series of plots are remarkably consistent and definite but not congruent, although the values for the 1800 series are generally lower than those for the 600 series. Evidently the annual variations in nitrogen content of the grain favored the 600 series of plots, which were cropped in the odd-numbered years. Nevertheless, the effect of the soil treatments on the nitrogen values for both series of plots was surprisingly similar. Wherever the wheat from one series shows

a difference in nitrogen content for any particular treatment, that from the other series indicates a similar change. The conformity is close enough to warrant consideration of an average of the two, which is presented at the bottom of

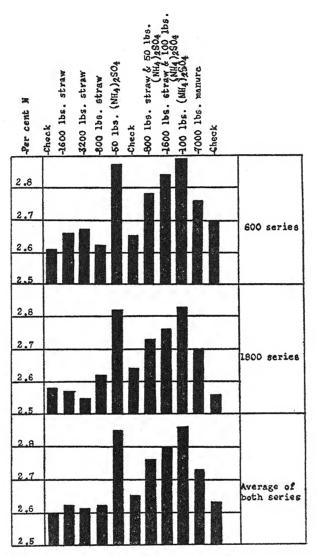FIG. 1. NITROGEN CONTENT OF GRAIN FROM PLOTS OF THE 600 AND 1800 SERIES AND AVERAGES OF BOTH SERIES

figure 1 and which shows that there was very little difference in the nitrogen content of the grain from the plots receiving straw alone and that from the check plots. This indicates that the added straw even in quantities of 3200 pounds per acre had no depressing effect on the nitrogen content of the grain.

On the other hand, the addition of nitrogen fertilizer or manure resulted in the production of grain with a higher nitrogen content. The effect of applications of 50 pounds and of 100 pounds per acre of ammonium sulfate alone was most pronounced in increased nitrogen content of the grain. Applications of straw with ammonium sulfate and of manure affected the grain in an intermediate manner but in proportion to the amount of nitrogen added. The grain from the plots receiving 100 pounds of ammonium sulfate with 1600 pounds of straw per acre, for instance, contained a slightly larger percentage of nitrogen than the grain from the plots receiving 50 pounds of ammonium sulfate with 800 pounds of straw per acre.

TABLE 4

Annual and average straw yields per acre for the 600 and 1800 plot series from 1923 to 1940*

PLOT	603-1812	604-1813	605-1814	606-1815	607-1816	608-1817	609-1818	610-1819	611-1820	612-1821	613-1822	AVERAGE OF CHECKS
	lbs.	lbs.	lbs.	lbs.	lbs.	lbs.	lbs.	lbs.	lbs.	lbs.	lbs.	lbs.
1923	2,480	2,320	2,400	2,540	2,580	2,380	2,600	2,700	2,840	2,300	2,480	2,447
1924	1,550	1,470	1,430	1,440	1,560	1,610	1,510	1,490	1,400	1,540	1,730	1,630
1925	1,230	1,140	1,060	1,210	1,510	1,160	1,260	1,520	1,460	1,180	1,030	1,140
1926	1,130	1,310	1,200	1,240	1,280	1,380	1,230	1,340	1,120	1,270	1,530	1,347
1927	2,420	2,300	2,210	2,260	2,510	2,100	2,430	2,680	2,860	2,400	2,260	2,260
1928	2,550	2,170	2,310	2,110	2,280	2,400	2,770	3,010	2,900	2,760	2,910	2,620
1929	750	690	700	640	710	700	690	740	730	590	600	683
1930	430	340	400	390	430	520	560	550	520	490	470	473
1931	590	500	390	410	350	460	350	430	400	390	470	507
1932	820	780	780	740	790	820	940	920	810	900	770	803
1933	680	720	630	730	720	820	780	820	770	870	780	760
1934	1,880	1,920	2,649	1,280	2,570	2,048	1,690	1,770	1,600	1,843	1,850	1,926
1935	2,180	2,360	2,340	2,140	2,020	2,220	2,180	2,380	2,240	2,460	2,300	2,233
1936	1,060	1,080	1,280	980	920	880	1,040	1,060	1,020	1,060	960	966
1937	224	334	344	354	274	304	274	414	354	374	354	284
1938	2,220	2,930	2,510	2,160	2,000	2,160	2,520	1,890	1,700	1,910	1,580	1,987
1940	862	943	1,024	781	943	889	1,158	1,104	929	1,212	943	898
Av.....	1,356	1,371	1,392	1,291	1,379	1,344	1,414	1,460	1,391	1,385	1,354	1,351

* Series 600 was cropped in odd-numbered years, and series 1800 in even-numbered years. See table 2 for treatments.

Under the climatic conditions of this experiment, when soil moisture was a limiting factor in crop production, any addition of nitrogen caused an increase in protein content of the grain, but over the experimental period the average yields of wheat on nitrogen-treated plots were not correspondingly increased. Since both series of plots behaved similarly in this regard, the results may be considered significant. The average yield for the plots receiving 100 pounds per acre of ammonium sulfate alone was 14.8 bushels per acre. The amount of nitrogen added per acre biennially in this case was 21.0 pounds. The plot receiving 50 pounds of ammonium sulfate per acre yielded an average of 14.4 bushels per acre. The nitrogen added as fertilizer in this case was 10.5 pounds.

There was a better recovery per unit of nitrogen added in the latter instance, but the amount of nitrogen removed in the grain from those plots exceeds that removed from the check plots by only one or two pounds annually. Evidently not all the nitrogen added to the soil as ammonium sulfate was recovered in the grain.

Yields of straw

The annual total and average weights of straw produced per acre on different plots are recorded in table 4.
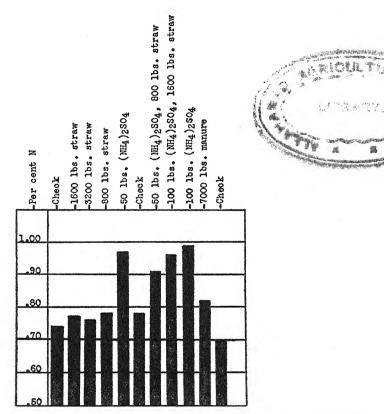
Fig. 2. Average Nitrogen Content of the Straw of Four Crops during 1923–1940 from Plots of the 600 and 1800 Series

Plots receiving the larger quantities of nitrogen fertilizer gave the higher yields of straw. All the fertilized plots, except those treated with 800 pounds per acre of straw alone, yielded more straw on the average than the checks. The reason for this behavior is not clear.

Nitrogen content of the straw

The nitrogen content of the straw of four crops was determined, and the results are presented in figure 2. These data reveal that the nitrogen content

was strongly affected by the amount of nitrate-nitrogen present in the soil at the beginning of the crop season, as shown in figure 3. In fact, the variations in the values for the nitrogen content of the grain and straw are almost identical with the variations in nitrate-nitrogen values in figure 3. This indicates that nitrogen added to the soil, even in a semiarid region, has a very definite effect on the nitrogen content of both grain and straw, especially of straw. As the tonnage of straw increased or decreased from year to year because of differences in growing conditions, the nitrogen content of the straw decreased or increased
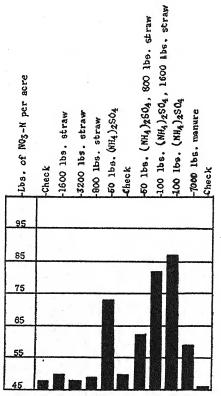
Fig. 3. Average Nitrate Nitrogen in Soil Sampled to Depth of Moisture Penetration in Plots of the 600 and 1800 Series during 1923–1933

inversely; that is, the total amount of nitrogen taken up by the plant tended to remain relatively constant from year to year. This resulted in marked annual variation in the percentage of nitrogen in the straw for all plots regardless of treatment, although straw from plots well supplied with nitrogen contained more of this element than straw from plots with small amounts of available nitrogen.

Available moisture in the soil

The data in table 5, giving the amount of moisture in the soil at the beginning of the crop year, show some variation between the two series of plots so far as

moisture retention is concerned, and also that no particular treatment produced consistent effects on the amount of moisture retained in the soil. The variation in moisture content from plot to plot was small, but it is important to note that the treated plots produced more straw than the check plots and an equal amount of grain. This emphasizes the point that an increase in the fertility of a soil or in the organic matter content generally resulted in a decrease in the water requirement of the crop being grown.

TABLE 5

Soil moisture in acre-inches on the plots of the 600 and 1800 series sampled in the spring of each crop year from 1923–1940

PLOT*	1923	1925	1927	1929	1931	1933	1937	AVERAGE
603	5.83	6.65	9.72	3.80	4.56	6.02	2.18	6.46
604	6.10	6.40	9.47	3.76	4.50	5.76	2.56	6.43
605	5.70	6.35	9.48	3.74	4.40	5.42	2.80	6.31
606	6.23	6.78	9.16	3.70	4.40	6.48	2.52	6.55
607	6.15	6.47	9.53	3.80	4.52	6.15	2.59	6.54
608	6.23	6.52	9.37	3.82	4.56	6.38	2.38	6.54
609	5.91	6.39	9.23	3.52	4.38	5.99	2.13	6.26
610	6.45	6.58	9.30	3.81	4.49	6.16	2.54	6.55
611	6.30	6.26	9.24	3.71	4.43	5.76	2.56	6.38
612	5.65	6.10	9.19	3.50	4.28	5.92	2.15	6.13
613	6.00	6.23	9.33	3.67	4.62	5.90	2.69	6.41

PLOT*	1924	1926	1928	1930	1932	1938	1940	AVERAGE	AVERAGE OF BOTH SERIES
1812	....	6.90	9.96	1.98	6.67	6.91	6.81	6.54	6.50
1813	7.28	6.90	9.41	2.35	6.89	7.05	7.12	6.71	6.57
1814	7.52	6.49	9.55	2.21	6.09	7.30	6.92	6.58	6.50
1815	7.52	6.72	9.77	2.32	6.59	6.88	6.63	6.63	6.59
1816	7.62	6.44	9.34	2.27	6.65	6.68	6.49	6.49	6.52
1817	7.70	6.64	10.03	2.47	6.81	7.26	6.81	6.81	6.68
1818	7.62	6.40	9.33	2.72	7.02	7.08	6.72	6.72	6.49
1819	7.75	6.51	9.57	2.44	7.41	6.87	6.78	6.78	6.67
1820	7.52	6.87	9.58	2.41	6.48	6.41	6.60	6.60	6.49
1821	7.62	6.74	10.18	2.26	6.76	7.37	6.90	6.90	6.52
1822	7.74	6.67	9.64	2.51	6.92	7.06	6.76	6.76	6.59

* See table 2 for treatments.

Nitrate-nitrogen content of soil

The amount of nitrate-nitrogen in pounds per acre to the depth of water penetration, generally 4 of more feet, was determined at the beginning of the crop year for each plot from 1922 to 1933 inclusive. Averages of these data are shown graphically in figure 3. The amount of available nitrogen was generally greater in the fertilized soils than in the nonfertilized soils, and also in the soils to which ammonium sulfate alone had been added than in soils to which the same treatment with straw had been made. Judging from the crop

behavior, however, the straw-treated plots released the nitrates to the plants at a slower rate and over a longer period than did the plots to which ammonium sulfate alone had been added. As a general rule, this is desirable, since it does not unduly stimulate profuse spring growth which cannot be satisfactorily matured on the amount of stored soil moisture available for the entire growing period. Moreover, straw treatments may be an important factor in maintaining the organic matter of the soil.

Changes in organic carbon content of the soil

If appreciable quantities of organic substances are added to a soil after it has reached equilibrium with the climate and with tillage and cropping practices, a

TABLE 6

Organic carbon in soil of plots of the 600 and 1800 series in 1922 and 1940 with loss or gain for each plot and average loss or gain for each treatment

Acre = 2,000,000 pounds soil

PLOT*	1922	1940	GAIN OR LOSS		PLOT*	1922	1940	GAIN OR LOSS		AVERAGE GAIN OR LOSS, BOTH SERIES	CARBON CONTRIBUTED BY TREATMENTS†
	per cent	*per cent*	*per cent*	*lbs./A.*		*per cent*	*per cent*	*per cent*	*lbs./A.*	*lbs./A.*	*lbs./A.*
603	.6326	.5629	−.0697	−1,394	1812	.5418	.5463	+.0045	+90	−652	...
604	.5662	.5892	+.0230	+460	1813	....	.6268	....	....	+460	+1,340
605	.5893	.6237	+.0344	+688	1814	.5309	.6491	+.1182	+2,364	+1,526	+2,406
606	.5616	.5480	−.0136	−272	1815	.4840	.5425	+.0585	+1,170	+449	+1,329
607	.5559	.5632	+.0073	+146	1816	.5170	.5920	+.0750	+1,500	+823	+1,703
608	.5509	.4852	−.0657	−1,314	1817	....	.5334	....	....	−1,314	....
609	.5697	.5376	−.0321	−642	1818	.5812	.5680	−.0132	−264	−453	+427
610	.5627	.5830	+.0203	+406	1819	.5001	.6021	+.1020	+2,040	+1,223	+2,103
611	.5475	.5400	−.0075	−150	1820	....	.5402	....	....	−150	+730
612	.5449	.6478	+.1029	+2,058	1821	.5245	.6682	+.1437	+2,874	+2,466	+3,346
613	.5528	.5340	−.0188	−376	1822	.6242	.5540	−.0702	−1,404	−890	....

* See table 2 for treatments.
† Based on average loss of 880 pounds per acre for five check plots.

relative increase in organic carbon content would be expected, but if cropping is continued without such additions, the organic matter of the soil may become seriously depleted.

Organic carbon relationships in the soil should be discussed from two viewpoints: first, the changes in organic carbon content of the soils as indicated by the samplings made in 1922 and in 1940; and second, the gains or losses of carbon in the treated soils as compared with the untreated soils. The analytical data are given in table 6.

It is apparent that the fertilized plots have maintained the organic matter at a higher level than the check plots. The soil of the plots that received straw or manure contained a larger quantity of organic carbon in 1940 than they did in 1922, except plots 606, 609, and 1818, which received only 800 pounds of

straw per acre in alternate years. A slight increase in organic carbon was also brought about by the treatments of 50 pounds per acre of ammonium sulfate alone, but these gains are small and may be within experimental error. In general, the gains resulting from comparable treatments were slightly greater in the 1800 series of plots than in the 600 series, but the trends appear to be the same. Unfortunately the three missing samples for 1922 made complete comparison impossible. These samples had been stored in metal tubes in a moist condition over a period of time. The metal containers had corroded and, therefore, it was considered advisable to discard the soil samples.

An analysis of the organic carbon data by the chi-square method shows that the odds against these differences in organic carbon content occurring by chance are more than 19:1. Since the chi-square value is 3.989, it can be accepted that the various treatments did cause significant changes in the organic carbon content of this semiarid soil. With a definite correlation existing between the data from identical treatments of the plots in the two series, the average values for organic carbon show that in all cases where organic residues or fertilizers were applied, the supply of soil organic matter was maintained better than in the check plots. Six of the treatments brought about an actual increase in organic matter. The additions of 800 pounds of straw per acre alone or with 50 pounds of ammonium sulfate, and of ammonium sulfate alone, were least effective in this respect. The comparative increases in organic matter that appear to have resulted from the various amounts of organic residues with and without nitrogen fertilizers are shown in table 6 in terms of organic carbon.

The data do not show any pronounced advantages for manure over straw in the production of soil organic matter when comparable quantities of nitrogen and dry matter are considered. The application of 1600 pounds of straw with 100 pounds of ammonium sulfate caused a greater increase in the amount of carbon retained in the soil than the 1600 pounds of straw applied alone, and was nearly as effective as the 3200 pounds of straw applied alone. This agrees generally with the reports of other investigators (12, 19) who have found that there is a definite relationship between nitrogen and carbon in soil organic matter found under specific climatic conditions, and, therefore, the nitrogen content of the soil must be increased before any appreciable additional amount of carbon can be retained in the form of organic matter. The fact that more carbon was fixed in the plots receiving 3200 pounds of straw alone per acre than in those receiving 1600 pounds of straw and 100 pounds of ammonium sulfate per acre does not conform strictly with the carbon-nitrogen relationship theory. It is possible, however, that the heavy application of straw without supplemental nitrogen caused a greater atmospheric nitrogen fixation by soil microorganisms than did the lighter straw treatments. Evidently the heavy straw treatment resulted in a larger amount of soil nitrogen than the lighter straw treatments, as may be noted from the data in table 7. This larger amount of nitrogen occurred regardless of the fact that no significant differences were found in the quantities of nitrogen removed by the crops on the various plots.

It is likely that the addition of highly carbonaceous materials to a semiarid

soil has the effect of reducing the supply of available nitrogen during the fallow year, because the supply must be used over and over again by the microorganisms to break down the relatively large volume of added organic residue. This process, in reality, provides a storehouse for nitrogen during the fallow year, and this nitrogen acts as a secondary factor in retaining some of the carbon as soil humus.

Changes in nitrogen content of the soil

Table 7 presents the analytical data on the nitrogen content of the soils from both series of plots for the 1922 and 1940 samplings. With but two exceptions, all of the soils have suffered a loss in total nitrogen during the experi-

TABLE 7

Nitrogen in soil of plots of the 600 and 1800 series in 1922 and 1940 with loss or gain for each plot and average loss or gain for each treatment

Acre = 2,000,000 pounds soil

PLOT*	1922	1940	GAIN OR LOSS		PLOT*	1922	1940	GAIN OR LOSS		AVERAGE GAIN OR LOSS, BOTH SERIES	NITROGEN CONTRIBUTED BY TREATMENTS†
	per cent	per cent	per cent	lbs./A.		per cent	per cent	per cent	lbs./A.	lbs./A.	lbs./A.
603	.0727	.0557	−.0170	−340	1812	.0618	.0598	−.0020	−40	−190	....
604	.0653	.0570	−.0083	−166	1813	.....	.0656	.....	...	−166	+77
605	.0649	.0644	−.0005	−10	1814	.0651	.0670	+.0019	+38	+14	+257
606	.0667	.0560	−.0107	−214	1815	.0657	.0584	−.0073	−146	−180	+63
607	.0674	.0570	−.0104	−208	1816	.0669	.0631	−.0038	−76	−142	+101
608	.0657	.0509	−.0148	−296	1817	.....	.0597			−296	....
609	.0668	.0584	−.0084	−168	1818	.0734	.0650	−.0084	−168	−168	+75
610	.0717	.0623	−.0094	−188	1819	.0668	.0643	−.0025	−50	−119	+124
611	.0700	.0565	−.0135	−270	1820	.....	.0596	.....	...	−270	−27
612	.0667	.0663	−.0004	−8	1821	.0643	.0681	+.0038	+76	+34	+277
613	.0673	.0581	−.0092	−184	1822	.0733	.0555	−.0178	−356	−270	....

* See table 2 for treatments.

† Based on average loss of 243 pounds per acre for five check plots.

mental period, those of the 600 series having lost more than those in the 1800 series. The data from the two series, however, exhibit the same general trends. The loss in soil nitrogen was generally inversely proportional to the amount of organic residue and nitrogen applied.

The reduction in the loss of soil nitrogen resulting from various treatments may be considered a gain in soil nitrogen as compared to the conditions prevailing in the check plots. This gain, as in the case of carbon, was influenced by the amount of organic residue added. According to Waksman and Hutchings (22), certain forms of organic residues are more effective than other forms in preserving the nitrogen in the soil. The manure treatment in this case, however, showed no appreciable advantage over the treatment of 3200 pounds of straw per acre. The addition of ammonium sulfate to the straw appeared to have a tendency to

increase the effectiveness of the treatment. The amounts of nitrogen contributed by the two treatments showing actual gains as well as the loss shown by the treatment with 100 pounds of ammonium sulfate are small and may be within the experimental error.

One way of accounting for the apparent gains in nitrogen from the straw and manure treatments is by assuming that fixation of free nitrogen took place. The gains obtained are proportional to the amount of carbon added in the form of organic residue, and the carbon-nitrogen ratios remained generally the same as may be noted in table 8. Greaves (11) pointed out that straw is more favorable to fixation of free nitrogen than is manure. This may explain why the heavy application of straw was more useful per unit of material added than was manure in increasing the nitrogen content of the soil. The gains in soil nitrogen

TABLE 8

Carbon-nitrogen ratios in soil of plots of the 600 and 1800 series in 1922 and 1940, and the average ratio in soils receiving identical treatments in both series

PLOT*	1922	1940	PLOT*	1922	1940	AVERAGE OF BOTH SERIES	
						1922	1940
603	8.7	10.1	1812	8.4	9.1	8.5	9.6
604	8.7	10.3	1813	...	9.6	...	10.0
605	9.1	9.7	1814	8.2	9.7	8.6	9.7
606	8.4	9.8	1815	7.4	9.3	7.9	9.6
607	8.3	9.9	1816	7.8	9.4	8.0	9.7
608	8.4	9.5	1817	...	8.9	...	9.2
609	8.5	9.2	1818	7.9	8.7	8.2	9.0
610	7.9	9.4	1819	7.5	9.4	7.7	9.4
611	7.8	9.6	1820	...	9.1	...	9.4
612	8.2	9.8	1821	8.2	9.8	8.2	9.8
613	8.3	9.2	1822	8.5	10.00	8.4	9.6

* See table 2 for treatments.

were accompanied by corresponding gains in organic carbon. Small changes in these two constituents, particularly if the changes of the two are in opposite directions, would be reflected by marked differences in carbon-nitrogen ratio. As indicated by the data in table 8 these ratios have increased somewhat uniformly for all treatments during the experimental period. The increase applies also to the check plots, indicating that the untreated soils lost nitrogen more rapidly than organic carbon. This fact and the fact that the loss of nitrogen was greatly reduced by heavy applications of straw indicate that the utilization of straw in wheat production on semiarid soils appears to have practical aspects in maintaining soil organic matter and nitrogen.

The possibility of increased fixation of free nitrogen in the presence of highly carbonaceous residues in the soil has been mentioned, but microbiological data to confirm this hypothesis are lacking. If fixation of free nitrogen was active in the soils under investigation and was stimulated by an abundance of highly

carbonaceous substances, there is a possibility that substantially heavier applications of straw than the quantities generally produced by a wheat crop on semiarid soils might promote the proper maintenance of organic matter and nitrogen in these soils. If repeated applications of large quantities of straw should eventually cause a marked widening of the carbon-nitrogen ratio of the soil organic matter, however, a reduction in wheat yields might result.

No appreciable difference in wind and water erosion on the variously treated plots has been observed during the summer-fallow year, although slight differences in soil structure have been noted in recent years. The soil was slightly more cloddy and brown in the plots receiving the heavy applications of organic residues.

SUMMARY

The results of a study from 1922 to 1940 of the organic residue and nitrogen fertilizer treatments applied in alternate years to each of two series of field plots established at the Adams Branch Station in 1922 may be summarized as follows:

Thus far the soil treatments have resulted in no outstanding increase or decrease in wheat yields and have not affected the bushel weight of the grain.

The nitrogen content of the wheat was increased by the manure treatment, by treatments of ammonium sulfate alone, and by treatments of straw with ammonium sulfate. Grain from the plots receiving ammonium sulfate alone had the highest nitrogen content, followed in descending order by the grain from treatments of 100 pounds ammonium sulfate with 1600 pounds of straw, 50 pounds of ammonium sulfate with 800 pounds of straw per acre, and of manure alone.

The yields of straw were greatest on the plot receiving 100 pounds of ammonium sulfate with 1600 pounds of straw per acre, followed in order by the treatments of 50 pounds of ammonium sulfate with 800 pounds of straw, 3200 pounds of straw alone, 100 pounds of ammonium sulfate alone, 7000 pounds of manure, 50 pounds of ammonium sulfate alone, 1600 pounds of straw alone, and 800 pounds of straw alone.

The nitrogen content of the straw followed the same order as the nitrogen content in the grain.

The amount of nitrate-nitrogen in the soil on different plots at the beginning of the crop season varied in the same way as the nitrogen content of the wheat grown on each plot, indicating that a direct relationship existed between available nitrogen in the soil and the nitrogen content of the grain.

On the basis of averages of the two series of plots, all treatments increased the organic carbon content of the soil, except the treatment of 100 pounds per acre of ammonium sulfate alone, and that of 50 pounds ammonium sulfate with 800 pounds of straw. Manure caused the greatest gain in organic carbon, followed by the other treatments in the following order: 3200 pounds of straw, 1600 pounds of straw with 100 pounds of ammonium sulfate, 50 pounds of ammonium sulfate alone, 1600 pounds of straw, and 800 pounds of straw alone.

All but two plots lost nitrogen during the experimental period. The nitrogen content of the soil was maintained at a higher level in the fertilized plots than in the nonfertilized plots, except in the plot receiving 100 pounds per acre of ammonium sulfate alone in alternate years. The efficiency of different treatments in maintaining the nitrogen level in the soil was in the following descending order: 7000 pounds of manure, 3200 pounds of straw alone, 1600 pounds of straw with 100 pounds of ammonium sulfate, 50 pounds of ammonium sulfate alone, 1600 pounds of straw alone, 800 pounds of straw with 50 pounds of ammonium sulfate, and 800 pounds of straw alone.

The carbon-nitrogen ratio of the soil organic matter increased in every plot regardless of treatment.

The results obtained indicate that applications of straw alone in amounts equivalent to or larger than those supplied by normal wheat crops are helpful in maintaining soil organic matter and nitrogen under a system of wheat farming on semiarid soils. Repeated applications of straw in quantities considerably exceeding those produced by average wheat crops may have a tendency to cause continued widening of the carbon-nitrogen ratio of the soil organic matter and eventually result in reduced supplies of available nitrogen and decreasing wheat yields.

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RELATION OF MOISTURE TENSION TO HEAT TRANSFER AND ELECTRICAL RESISTANCE IN PLASTER OF PARIS BLOCKS

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Soil investigators, particularly in regions where irrigation is a common practice, are realizing more and more the importance of associating moisture changes in soils with changes in energy levels of the soil moisture. Numerous methods have been proposed for following soil moisture changes *in situ* by means of instruments. A recent publication (8) reviews the literature on these methods and discusses the application and limitations of certain of the more important of the methods to field practice. Most methods employed have not been able to measure directly the security with which the water is held in the soil, that is, the soil moisture tension. The tensiometer method has accomplished this objective, but is limited to tensions below 0.85 atmosphere. Certain methods employing moisture measuring units made of paster of paris have been shown to be useful in following moisture changes in the higher tension ranges, but the instruments employed in these methods have been calibrated for each soil in terms of moisture percentage rather than moisture tension. It is the purpose of this paper to show the relation of heat transfer and electrical resistance in plaster of paris blocks to the tension of the water in the blocks. The possibilities of using these methods as a means of measuring soil moisture tension over the entire range of moisture available to plants will be discussed.

Many attempts have been made (8) to follow changes in soil moisture by measuring the electrical resistance between two electrodes placed in the soil. A more successful modification of this principle was introduced by Bouyoucos and Mick (3), who cast the electrodes in a plaster of paris block (hereinafter called "Bouyoucos block"). The electrical resistance between the electrodes is a direct function of the moisture content of the block (when temperature and other variables are held constant) and, assuming the block to be in moisture equilibrium with its surroundings, indirectly a function of the moisture content of the soil. Anderson and Edlefsen (1, 2, 5, 6) have made extensive studies on this method for measuring soil moisture and make the statement (1) that this unit "should not require a separate calibration for each soil, since it probably measures the tightness with which water is held." They reason that "at the permanent wilting percentage of all soils the plaster of paris blocks should all have the same electrical resistance. Likewise, at the moisture equivalent of all soils the blocks should all have the same electrical resistance. . ." If this is true, then it follows that once the units have been calibrated against moisture tension, it should be possible to apply them to any soil regardless of texture,

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provided no other external factors are involved. Jamison made such a calibration for the relation of moisture tension to the electrical resistance in Bouyoucos blocks, when the blocks were surrounded by soil. For obtaining equilibrium at the various tensions, he used a suction method at low tensions and a centrifugal method at higher tensions. His data are given in a paper by Cummings and Chandler (4).

Another method for following changes in soil moisture is the thermal method proposed by Shaw and Baver (11, 12). They have established that heat transfer in soils is a function of the soil moisture content. Lack of extensive field use of this method has been chiefly due to the difficulty of constructing a suitable thermal unit. Johnston (7) suggested the use of a plaster of paris jacket which would absorb the heat produced by the heating element. The results of his work indicate that comparable readings can be obtained at the "field capacity" and the wilting percentage on two soils having somewhat different moisture-holding characteristics. The plaster of paris jacket eliminated unit-soil contact difficulties which were present in the original design (11, 12). Using plaster of paris as the heat-absorbing medium, Shaw[2] later constructed a unit which, because of its design, was particularly well suited to the study reported in this paper. In the present studies, relationships between moisture tension and the electrical resistance of Bouyoucos blocks and the heat transfer from the Shaw-Baver thermal units were investigated by means of the pressure-membrane technique proposed by Richards (9).

MATERIALS AND METHODS

Details of the construction of Bouyoucos blocks are available in the literature (1, 3). Those used in this study and the portable conductivity bridge for resistance measurements were obtained commercially.[3] The thermal units were constructed in this laboratory. A length of enamelled 36-gauge copper magnet wire having a resistance of 10 ohms when immersed in water at a temperature of 25°C. was wrapped on a mica mounting approximately $1\frac{1}{4}$ inches square and $\frac{1}{32}$ inch thick. This assembly constituted the heating element. The two ends of the magnet wire were soldered to insulated copper leads, and all bare portions were insulated with clear lacquer. The heating elements were then clamped rigidly in a form and embedded in plaster of paris. To obtain uniformity in pore size, six units were poured simultaneously from the same plaster mix. Two pourings were necessary; the first secured the lead wires and heating element, and the second completed the bottom half-inch of the unit after removal of the clamp. The final dimensions of the thermal unit were $2\frac{1}{2}$ by $1\frac{3}{4}$ by $1\frac{1}{2}$ inches. A moisture meter designed especially for use with the Shaw-Baver themal units was used.[4]

The pressure membrane extraction apparatus designed by Richards (9) was used with some slight modifications to obtain tension ranging from 1 to 15

[2] Byron Shaw, unpublished data.

[3] Wood and Metal Products Company, Bloomfield Hills, Michigan.

[4] Lent to us by Leeds and Northrup Company, Philadelphia.

atmospheres. The cylindrical section of the extraction cell was 4 inches in height. (A section 2 inches in height has been used recently and is recommended because of its adaptability in the application of a differential pressure of 5 pounds per square inch.) Twelve spark plugs mounted in the sides of this cylindrical section (fig. 1) provided convenient insulated connections to the units and were capable of withstanding the required pressure of 220 pounds per square inch. A cylinder of nitrogen gas, with a pressure regulator and gauge, was used to obtain the differential pressures necessary in the various tensions.
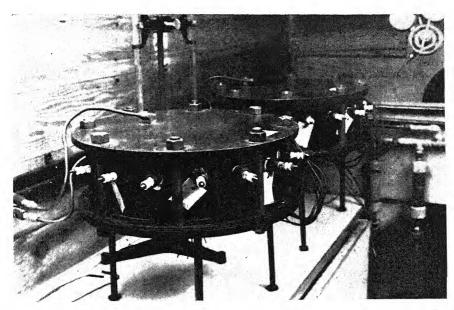
FIG. 1. GENERAL VIEW OF PRESSURE-MEMBRANE APPARATUS, SHOWING SPARK PLUGS INSTALLED AS BINDING POSTS

Before installation in the extraction cell the plaster units were immersed in distilled water and left for several hours in an evacuated container. The leads from the units were soldered to the spark plug terminals and lacquered to prevent short circuits resulting from condensation of moisture on the inside wall of the cylindrical section. The entire apparatus was kept in a room in which the temperature was closely controlled ($19.5 \pm 0.25°C$.). The Visking[5] membrane upon which the units were mounted was hydrated after installation in the extraction apparatus. (It was later found that the installation of a pre-hydrated Visking membrane was more satisfactory, for reasons discussed later.) The units were bonded to the membrane by brushing fresh plaster of paris in the desired position on the membrane, and then placing the units in the fresh plaster of paris before it had set, thus ensuring good contact. The arrangement and

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[5] Brand name of cellulose sausage casing, product of the Visking Corp., Chicago, Illinois.

the method of installing the units in the extraction cell are shown in figure 2. A differential pressure of 5 pounds per square inch was applied to the units, in the manner suggested by Richards and Weaver (10), to eliminate the possibility of poor contact resulting from membrane shrinkage.
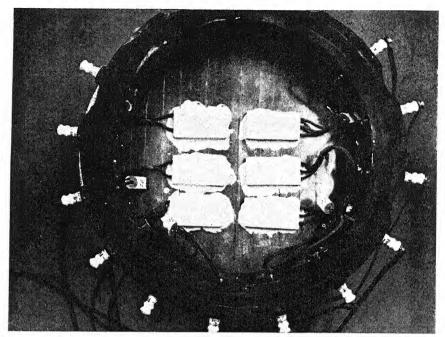
FIG. 2. INSIDE VIEW OF EXTRACTION CELL, SHOWING METHOD OF INSTALLING UNITS

EXPERIMENTAL RESULTS AND DISCUSSION

The curve presented in figure 3 shows the results obtained when the resistance of six Bouyoucos blocks is plotted against moisture tension. It is apparent that the resistance increases continuously throughout the range of tension from 0 to 15 atmospheres. Between 0 and 4 atmospheres the rate of increase $\dfrac{d\,(\log R)}{dt}$ is greater than that at the higher tensions. This particular characteristic of the block will be discussed later in connection with similar results obtained with the thermal units. It is interesting to note (fig. 3) that the points on the graph corresponding to the various tensions are well grouped, indicating good agreement between readings of the individual units. Inasmuch as the six units represented in figure 3 were selected at random from a large number, it is to be expected that the tension-resistance relationships of any other lot would be similarly grouped. The calibration of approximately 30 additional units has verified this expectation.

There are, however, several factors to be considered in the determination of the tension-resistance relationships for the Bouyoucos block by the pressure-

membrane technique (9). · Cummings and Chandler (4) have suggested that variability in resistance may be due to the fact that the conductance path of the electrical current is partly outside the block. Anderson and Edlefsen (1) have compared 2-electrode with 4-electrode plaster of paris blocks and found that the differences in resistance above the moisture equivalent are due to the relative magnitude of the current-flow outside the block. Slater (13) has alleviated this difficulty by constructing a unit in which the conductance path is confined
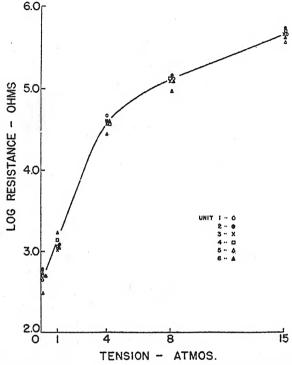
FIG. 3. RESISTANCE IN OHMS, OF BOUYOUCOS BLOCKS AT VARIOUS ATMOSPHERES OF TENSION

within the block through the location of one electrode centrally within a cylindrical screen, the screen itself forming the second or outer electrode.

The difficulties of external current flow are encountered with Bouyoucos units in contact with the Visking membrane. For this and other reasons which are discussed, the data in figure 3 must be taken as close approximations and not as exact values. As is seen in figure 2, the blocks were mounted with the flat side down. It was found that the resistance of blocks in equilibrium at any tension would register an increase when the unit-membrane contact was broken, that is, when the resistances of corresponding units were taken suspended in air. The magnitude of this increase varied between units, but in no case did it change considerably the over-all nature of the curve relating resistance to moisture tension. An increase in resistance occurring immediately after removal

of the unit from the membrane indicates that when the unit is in contact with the membrane the current follows a path of less resistance than that totally within the block. This path is probably through the Visking membrane and the 80-mesh copper screen support.

It should be emphasized that in using Visking membrane for this purpose, for obtaining sorption curves on soils, or for obtaining soil solutions it is highly important that the membrane be washed thoroughly in distilled water. The Visking membrane contains a considerable amount of salts and some soluble organic matter. This, of course, increases the salinity of a solution in contact with the membrane, and would tend to increase the electrical conductivity. An unwashed Visking membrane sorbs more water than one that has been washed. When an unwashed membrane is used in the determination of tension-moisture curves it is almost impossible to make a correction for the water held by the membrane. Prehydration and washing eliminates the wrinkling that occurs when the membrane is placed in the extraction cell and then hydrated. This makes for a better unit-membrane contact and removes most of the soluble materials. Nevertheless, the use of a washed membrane did not eliminate the problem of external current flow in the calibration of the Bouyoucos block. The external flow can be further reduced, however, by mounting the units on edge rather than with the flat side down. When thus mounted, any current flowing outside the block must traverse a path through air, a poor conductor. With the blocks mounted on edge, rather than on the side, the time required to establish moisture equilibrium at any tension is about twice as long and as a result the length of time required to complete a calibration usually exceeded the useful life (about 30 days) of the membrane. The data in figure 3 are for blocks placed flatside down, but the difference between these data and those obtained by placing blocks on edge did not exceed the experimental error.

At the beginning of this study it was noted that when blocks were saturated for 24 hours in distilled water and immediately subjected to an increased pressure of 1 atmosphere, the resistance decreased approximately 300 ohms. It is believed this decrease in resistance was due to the compression of entrapped air followed by a readjustment of moisture in the block. When the units were wetted under vacuum, the initial decrease in resistance was no longer apparent. Although the general shape of the curve was not affected, the manner in which the units were originally treated caused a displacement of the curve upward or downward. Units which were wetted under vacuum tended to have a slightly lower resistance.

It is apparent from the foregoing discussion that more study is needed before definite resistance values can be assigned to the blocks for any given tensions. Undoubtedly there is external current flow when the blocks are used in the field, perhaps more than when they are being calibrated in the laboratory. The resistance values obtained in the laboratory for resistance versus tension should be minimum values for the blocks when not in contact with soil, since external current flow tends to lower the actual resistance of the blocks.

The exact effects of different soils and varying concentrations of salts sur-

rounding the units are not known. It is believed by the suthors, however, that the values obtained would in general represent the relationship between the moisture tension and the electrical resistance in the block, provided the soil in contact with the block is low in salt. It should be pointed out, however, that the curves presented are for desorption only, and that it would be expected that the values would differ somewhat for sorption curves, since there apparently is not a unique relation between moisture content and moisture tension of porous bodies. The magnitude of hysteresis effects has not been evaluated in this study.
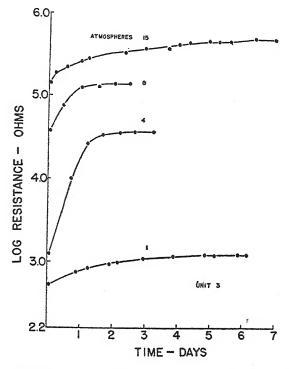
FIG. 4. TIME REQUIRED TO OBTAIN EQUILIBRIUM OF BOUYOUCOS BLOCKS AT
VARIOUS ATMOSPHERES OF TENSION

Typical curves shown in figure 4 indicate the time required for the units to approach equilibrium with each successive increase in tension. The equilibrium value at each pressure increment was returned to zero on the time scale in order to conserve space. The extraction pressure is indicated on each curve.

It is seen that 1 to 7 days is required to reach equilibrium. This does not necessarily mean that the units would lag this much if surrounded by soil in which the moisture was being removed by roots of actively transpiring plants. Only about one third of the surface of the unit is in contact with the membrane. If moisture were being removed from the entire surface area, the time required for the establishment of equilibrium would undoubtedly be considerably re-

duced. As indicated by the slope of the topmost curve in figure 4, equilibrium at 15 atmospheres of tension was never quite attained, the resistance increasing continuously. At the higher tensions a slight loss of moisture results in a large increase in resistance (as is shown in figure 6); it may be that the continued increase in resistance at 15 atmospheres was due to loss of moisture from the units by evaporation. That this loss was not of great importance is indicated by the equilibrium curves for 4 and 8 atmospheres of tension, which show that once equilibrium has been attained there is very little further change in resistance
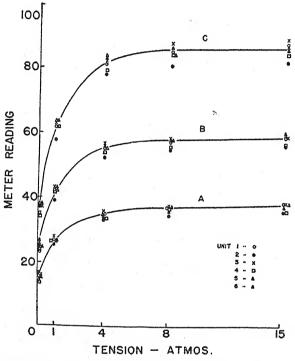
FIG. 5. METER READINGS OF THERMAL UNITS OBTAINED AT VARIOUS TENSIONS

(A) 0.32 ampere for 60 seconds; (B) 0.37 ampere for 60 seconds; (C) 0.42 ampere for 60 seconds.

over a period of 2 days. Without close control of temperature, this fact would not have been easily established, since the block resistance varies with temperature. When temperature corrections must be applied to the resistances it is difficult to ascertain when equilibrium has been established.

The relationship between moisture tension and meter readings for the thermal units is shown in figure 5. Curves A, B, and C represent the meter readings obtained after a current of 0.32, 0.37, and 0.42 amperes, respectively, had been passed through the heating element for 60 seconds. As with the Bouyoucos blocks, there was little difference in the behavior of the individual units; this is shown by the close grouping of points obtained under similar conditions of tension and heating.

It is interesting to note the rapid initial rise of the meter reading at tensions below 4 atmospheres and the abrupt leveling off which occurs at tensions above this value. As shown in figure 3, a somewhat similar break occurred in the calibration curve for the Bouyoucos blocks, although to a much less degree. It is apparent from curve B of figure 6 that very little water was removed at tensions above 4 atmospheres and virtually none above 8 atmospheres. The desorption curve on plaster of paris (A, fig. 6) also indicates that most of the water is held at tensions below 4 atmospheres, although there is an appreciable
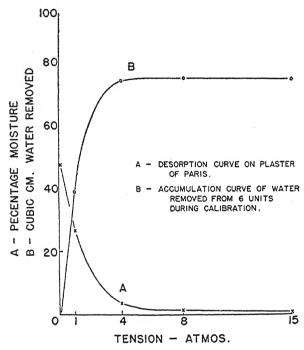
FIG. 6. (A) DESORPTION CURVE ON PLASTER OF PARIS; (B) AMOUNT OF WATER REMOVED FROM SIX BOUYOUCOS BLOCKS DURING CALIBRATION

loss over the entire range above 4 atmospheres which could not be detected by removal of water from the units. This is not particularly disturbing, since the physical properties of plaster of paris vary somewhat, depending on the manner of preparation and the purity of materials used. It is apparent from these data that the Bouyoucos blocks continued to register changes in resistance above 4 atmospheres of tension with very slight changes in the moisture content of the block. The thermal units, on the other hand, responded to changes in moisture content only so long as an appreciable loss of moisture took place. It should be pointed out that the inability of these specific thermal units to respond to tensions above 4 atmospheres does not necessarily place any limitations on this method for measuring soil moisture. It does indicate, however, that thermal units made with plaster of paris jackets, as were those used in this
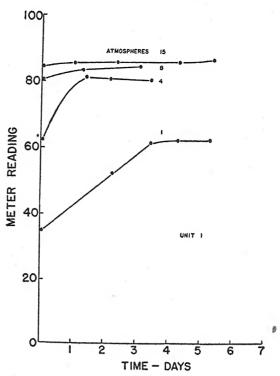
FIG. 7. TIME REQUIRED TO OBTAIN EQUILIBRIUM OF THERMAL UNIT AT VARIOUS TENSIONS
0.42 ampere for 60 seconds
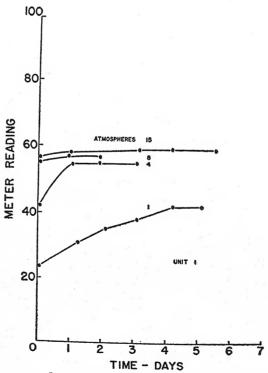
FIG. 8. TIME REQUIRED TO OBTAIN EQUILIBRIUM OF THERMAL UNIT AT VARIOUS TENSIONS
0.32 ampere for 60 seconds

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experiment, are not suited for measuring moisture tensions above 4 atmospheres. A porous medium having a pore-size distribution such that it could gradually release moisture over the 0–15-atmosphere range would undoubtedly produce more satisfactory results.

The curves shown in figures 7 and 8 are plotted in essentially the same manner as those previously mentioned and indicate the time required for the thermal units to reach equilibrium. The foregoing data indicate that the plaster of paris units exhibit definite moisture-tension characteristics on desorption in the absence of soil. Whether this relationship will still hold when the same technique is applied to units surrounded with various types of soil, is being studied at the present time.

SUMMARY

Calibration curves relating moisture tension to electrical resistance and heat transfer in plaster of paris blocks are presented.

The errors and difficulties encountered in making these calibration curves by means of the pressure-membrane technique are discussed.

A desorption curve on plaster of paris indicates that most of the moisture is held at tensions below 4 atmospheres.

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A PEDOLOGIC STUDY OF CALIFORNIA PRAIRIE SOILS

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The typical prairie soils were first described and separated as a great soil group by Marbut (13), who thought that they were unique to the prairie belt of the Middle West. There are, however, a considerable number of soils in California which are very similar to the prairie soils of the Midwest and which were classified later as prairie soils (21). The inclusion of these California soils among the prairie soils was based on a few soil properties which were considered typical for the midwestern prairie soils, namely, surface color—dark brown to black; structure—granular; reaction—slightly acid at the surface and leached of lime throughout the profile. This similarity between the midwestern prairie soils and the so-called California prairie soils is of a pedological interest for the reason that the soil-forming factors in the two regions differ considerably. These differences are as follows:

California prairie soils are not confined to grasslands; a considerable number are found under brush or forest with a dense brush undergrowth. The topography of California prairie soils is considerably more rolling and hilly than the midwestern prairie soils. Whereas the parent material of the California prairie soils consists of a great variety of rocks such as acid, basic, and metamorphic igneous rocks, sandstone, and shale, that of the midwestern prairie soils consists mainly of glacial till and loess. There is also an apparent difference in the climate of the two regions, particularly in the seasonal distribution of precipitation and winter temperatures. In California the precipitation is chiefly in the winter months, whereas in the Midwest the precipitation is distributed evenly throughout the year. Winter temperatures are considerably higher in California than in the Midwest.

Because of these differences in the soil-forming factors in the two regions, it was felt that a quantitative evaluation of several soil properties of the so-called California prairie soils and a comparison made with like properties of the midwestern prairie soils (from data reported by other investigators) may reveal the true degree of similarity between the soils of the two regions. Such an investigation will also make it possible (*a*) to determine what soil properties are common to all the prairie soils and (*b*) to establish the dominant properties of the soil-forming factors for the prairie soils as a whole.

THE SOILS STUDIED

The soils studied lie in a narrow belt on the coastward side of the Pacific Coast Ranges, from Santa Barbara north and in the region surrounding San

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Francisco Bay.   They are formed under a rainfall of 18 to 30 inches, considerable summer fog, and fairly low summer temperatures.   The surface soils are dark grayish brown to black, free of lime, and have a good granular structure.   The soil series studied were the Colma, Sweeney, Sheridan, Gleason, Cayucos, and Los Osos.   The locations of the profiles sampled are indicated in table 1.

TABLE 1

Description of profiles of California prairie soils collected for present investigation

SOIL TYPE	LOCATION	THICK-NESS OF PROFILE	PARENT MATERIAL	TOPOGRAPHY	VEGETATION	CLIMATE: RECORDS OF NEAREST STATION TO PROFILE (22)	
						Average rainfall	Temp-erature
		inches				*inches*	°F.
Sweeney clay loam	¾ mile north of Sharp Park alongside Sneath Road to Sharp Park, San Mateo County	0–32	Augite, olivine, and plagioclase basalt	Rolling to hilly	Grass and some shrubs	San Francisco 20.6* 1.46†	54.5* 58.7†
Sheridan sandy clay loam	1½ miles north of Coastwide Community Chapel in Montara, San Mateo County	0–30	Hornblende, bio-tite, quartz, granodiorite	Hilly to moun-tainous	Grass and shrubs		
Colma I sandy loam	1½ miles southwest of Colma, San Mateo County	0–18	Moderately con-solidated non-calcareous sandstone	Rolling to hilly	Grass and some shrubs		
Colma II sandy loam	30 yards north of Colma I profile	0–36	Moderately con-solidated cal-careous sand-stone	Rolling to hilly	Grass and some shrubs		
Gleason clay loam	12 miles northeast of Alturas on State Highway No. 8A, Modoc County	0–36	Acid andesite tuff	Hilly to moun-tainous	Grass and open timber	Alturas‡ 9.4* 3.3†	37.4* 60.1†
Cayucos sandy clay loam	200 yards south of Rodeo on U. S. Highway No. 40, Contra Costa County	0–36	Unconsolidated noncalcareous sandstone	Undulat-ing to rolling	Grass	Crockett 16.2* 1.11†	54.1* 65.2†
Los Osos sandy clay loam	About 2½ miles south of Wal-nut Creek, Contra Costa County	0–30	Moderately con-solidated non-calcareous sandstone	Undulat-ing to rolling	Grass	Walnut Creek 19.86* 1.31†	52.6* 69.4†

* October to April.
† May to September.
‡ The rainfall is probably greater at the location of the profile, for it is at a higher elevation than the station.

The profiles were sampled at 6-inch depth intervals.   In every case the lowest sample in the profile represents the loose bedrock.   All profiles were collected at the highest and flattest part of a ridge on rolling to hilly topography. The samples were air-dried, ground very lightly, and passed through a 2-mm. sieve, then thoroughly mixed and bottled.

EXPERIMENTAL RESULTS

pH values

The pH measurements were made with a Beckman pH meter on duplicate samples. The proportion of soil to water was 1:2. The results are recorded in tables 5 and 6. These results were compared with the pH of representative midwestern prairie soils (1, 2, 3, 13, 17), and the following common features were noticed to be present:

(a) In most of the soils, the pH increases with depth. As a rule, the pH of the surface is on the acid side; it becomes neutral to alkaline with depth. (b) The California prairie soils are less acid than the midwestern prairie soils, some even being neutral at the surface. (c) The range of variation in pH of both the surface and the subsoils is wide and is alike in both groups of prairies.

The wide range of variation in pH among these soils is probably brought about by variation in some of the soil-forming factors. Among the California prairies the most variable factor is the parent material. The higher pH of the Sweeney may be attributed to its highly basic parent material, and that of Colma II to its calcareous parent material. The variation in the pH among the midwestern prairies may be attributed to three soil-forming factors; namely, (a) variation in topography, the soils on the gentler slopes being more acid than those on the steeper slopes; (b) the variation in the time factor or "age" of the profile; the more acid soils have the "older" profiles, as measured by both the horizon development and the time since the retreat of the glaciers (15); and (c) variation in rainfall (17); the soils under a higher rainfall have lower pH values.

Total carbon, nitrogen, and organic matter

Total nitrogen was determined by the Kjeldahl method; total carbon was determined by the dry combustion method; and total organic matter of the soil was calculated from the total carbon (C $\times$ 1.742).

The results are recorded in table 2. These results were compared with the total carbon, nitrogen, and C/N ratios of representative midwestern prairie soils (12, 13, 17) and the following points were noted:

1. The values in each of the prairie groups show a wide range of variation; however, the average values of one group are almost equal to those of the other. 2. Total nitrogen, carbon, and organic matter decrease with depth, making a diffusion pattern of distribution. 3. The variation in these values among the soils decreases with increasing depth from the surface. 4. The C/N ratio in most of the prairie soils decreases with depth. The range of variation of this ratio among the soils is rather small. At the surface it ranges from 9 to 12, and at the lowest horizon, with the exception of the Gleason, from 5 to 7.

The wide range of variation in carbon, nitrogen, and organic matter among these soils is probably brought about by the variation in climate, and possibly by variation in parent material. The extent of the variation due to temperature

TABLE 2

Total carbon, nitrogen, and organic matter and C/N ratios of California prairie soils

SOIL	DEPTH	C	N	C/N	ORGANIC MATTER C × 1.742
	inches	per cent	per cent		per cent
Sweeney	0–6	3.09	0.287	10.8	5.39
	6–12	2.34	0.219	10.7	4.06
	12–18	2.08	0.173	12.0	3.62
	18–24	2.06	0.178	11.6	3.59
	24–30	1.38	0.135	10.2	2.40
	30–36	0.32	0.047	6.9	0.56
Sheridan	0–6	3.66	0.348	10.5	6.37
	6–12	2.65	0.261	10.2	4.62
	12–18	2.08	0.209	9.5	3.62
	18–24	0.76	0.100	7.6	1.33
	24–30	0.30	0.046	6.5	0.52
Gleason	0–6	2.03	0.179	11.4	3.54
	6–12	1.76	0.159	11.1	3.06
	12–18	1.46	0.136	10.7	2.54
	18–24	1.21	0.120	10.1	2.11
	24–30	0.99	0.102	9.7	1.73
	30–36	0.89	0.090	9.9	1.55
Cayucos	0–6	1.82	0.158	11.6	3.17
	6–12	1.00	0.096	10.5	1.74
	12–18	0.65	0.075	8.6	1.31
	18–24	0.49	0.059	8.3	0.85
	24–30	0.32	0.042	7.7	0.56
	30–36	0.15	0.026	5.7	0.26
Los Osos	0–6	1.21	0.130	9.2	2.11
	6–12	0.64	0.080	8.0	1.12
	12–18	0.55	0.057	9.6	0.96
	18–24	0.25	0.048	5.2	0.44
	24–30	0.07	0.015	4.7	0.12
Colma II	0–6	2.06	0.212	9.8	3.58
	6–12	1.60	0.144	11.1	2.79
	12–18	0.66	0.081	8.1	1.15
	18–24	0.74	0.096	7.7	1.29
	24–30	1.07*	0.091	....	....
	30–36	1.43*	.....	....	....
Colma I	0–6	1.99	0.199	10.0	3.47
	6–12	1.42	0.147	9.7	2.47
	12–18	0.54	0.072	7.5	0.94

* Lime present.

and rainfall for carbon and nitrogen was shown by Jenny (10). Among the California prairie soils the Sweeney, Sheridan, and the two Colmas are found

under conditions of highest rainfall and coolest summer temperatures; the Los Osos, under the warmest summer temperatures; the Cayucos and Gleason, under intermediate conditions. Among the midwestern prairie soils the northern prairie soils have higher values of C and N than the ones farther south (13). The extent of the variation in organic matter due to parent material may be a reflection of the variation in soil fertility brought about by the parent material. This is a suggestion which needs to be investigated further.

Mechanical Analysis

The fractions total sand, $< 2\mu$, and $< 1\mu$ in diameter were determined by the pipette method for mechanical analysis. From each of the soil samples used for the clay determinations the fraction $50-5\mu$ in diameter was extracted quantitatively, whereas the fraction $5-2\mu$ in diameter was calculated by difference. The results of these analyses are given in table 3. The distribution of the clay fraction with depth of a few midwestern (7, 13, 14) prairie soils is given in figure 1.

Mechanical analyses were also run on the $< 1\mu$ clay fractions which were extracted from the soils for total chemical analysis. The results are given in table 4.

From tables 3 and 4 and figure 1 it is possible to present the following observations:

1. With the exception of the Sheridan, all the prairies show, to various degrees, a maximum of clay content at some horizon below the surface. 2. The distance of the horizon with the maximum clay content from the surface of the soil is not constant; it ranges from 12 to 30 inches. This range is similar for both the Californian and the midwestern prairie soils. 3. The increase of clay content from the surface horizon to the maximum horizon varies greatly among these profiles, both in the absolute increase and in the rate of increase.

In the midwestern prairies this property has been used by Bray (4, 5, 6) and Norton (15) as a basis for grouping these soils in various age categories. The soils with the smallest maxima were considered the youngest profiles, and those with the greatest maxima, the oldest profiles. This assignment of "age" was consistent with the "age" as measured by glacial periods. This grouping, however, cannot be applied to the California prairie soils, for their parent material is not alike. This diversity of parent material is probably one of the important factors contributing to the variation in the absolute clay content and its distribution with depth.

The change with depth in the particle size distribution of the clay fractions $< 2\mu$ has been used by Steele and Bradfield (19) and by Bray (5) as a basis for detecting clay migration and horizon differentiation. Horizons below the surface soil which show a predominance of the finest clay particles may be considered as horizons of accumulation, whereas surface horizons which show a predominance of the coarser fractions of the clay may be considered horizons of eluviation.

Such a study of the particle size distribution of the clay fractions was undertaken in the present investigation to a limited extent; only the $< 2\mu$ and $< 1\mu$ clays were determined for all the profiles, and the composition of $< 1\mu$ clay

was determined for the Sweeney, Cayucos, Los Osos, and Sheridan.   Even such a limited study reveals that those horizons which possess the highest content of $< 2\mu$ clay also possess the highest content of the $< 1\mu$ clay.   This can be observed particularly in the Cayucos, Los Osos, Colma, and Gleason.   The smaller clay fractions (table 4) show a maximum of clay content at the 18–24-inch horizon in the Sweeney profile, whereas in the Sheridan profile the smaller fractions of the clay increase all the way to the disintegrated parent material.   This suggests, therefore, that the pattern of the clay distribution with depth is due, at least in part, to downward clay migration.

Cation-exchange studies

The exchange capacities and exchangeable bases of the soils and colloids were determined by the ammonium acetate method.   The results are reported in
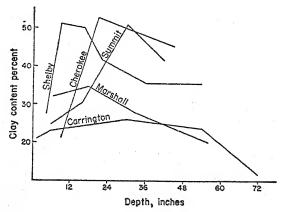
FIG. 1. RELATIONSHIP BETWEEN CLAY CONTENT AND DEPTH FOR A FEW MIDWESTERN PRAIRIE SOILS

tables 5, 6, and 7 and figure 2, from which the following observations may be made:

The exchange capacities of the Sweeney samples, both the whole soil and the colloids, are unusually high; probably they are the highest capacities ever reported for mineral soils.

The percentage composition of the exchangeable bases show the following relationships: (a) calcium plus magnesium constitute 92–98 per cent of the total bases; (b) per cent Ca^{++} decreases with depth in the Sheridan, Gleason, Cayucos, Colma I, and Colma II; remains about constant in the Los Osos; and increases very slightly in the Sweeney; (c) the distribution of Mg^{++} with depth is exactly the opposite of the Ca^{++} distribution.

In the Sweeney, Sheridan, Colma II, and the lowest horizons of the Los Osos, the sum of the bases exceeds the NH_4-exchange capacity.   However, in the Gleason, Cayucos, Colma I, and the upper three horizons of the Los Osos, the NH_4-exchange capacity exceeds the sum of the bases—the difference is assumed to represent exchangeable H^+.   Unpublished data indicate that the total exchangeable H^+ exceeds considerably this quantity, also that even in the soils which show excess bases over NH_4^+ adsorbed, the total exchangeable H^+ is very considerable.

TABLE 3
Mechanical analysis of California prairie soils

SOIL	DEPTH	FRACTIONS					$\frac{<1\mu}{<2\mu} \times 100$
		Fine gravel and sand 2.0–0.5 mm.	Silt 0.05–0.005 mm. (50–5μ)	Silt 0.005–0.002 mm. (5–2μ)	Clay < 0.002 mm. (<2μ)	Clay <0.001 mm. (<1μ)	
	inches	per cent	per cent	per cent	per cent	per cent	per cent
Sheridan sandy clay loam	0–6	54.70	16.91	5.81	22.58	19.36	85.8
	6–12	57.50	13.08	6.39	23.02	19.62	85.2
	12–18	58.10	12.81	6.45	22.64	19.43	85.8
	18–24	69.75	9.56	4.89	15.80	13.84	87.6
	24–30	71.99	14.82	0.91	12.28	10.67	86.9
Sweeney clay loam	0–6	47.87	12.90	5.88	33.35	28.42	85.4
	6–12	44.98	15.00	6.06	33.96	28.89	85.3
	12–18	42.75	17.58	5.63	34.04	29.72	87.4
	18–24	41.98	15.90	6.25	35.86	30.61	85.4
	24–30	46.28	14.77	7.56	31.39	27.00	86.1
	30–32	60.66	17.88	5.15	16.31	12.67	77.5
Gleason clay loam	0–6	46.08	21.00	8.83	24.09	18.56	77.0
	6–12	45.90	20.68	8.58	24.84	20.59	82.8
	12–18	44.22	21.60	8.64	25.54	21.05	82.3
	18–24	39.42	18.95	8.03	33.60	28.34	84.4
	24–30	33.29	22.30	6.12	38.29	31.04	81.2
	30–36	39.35	22.69	8.46	29.40	24.18	82.2
Los Osos sandy clay loam	0–6	52.33	21.61	5.04	21.02	18.55	88.2
	6–12	44.83	23.40	5.10	26.67	24.83	93.2
	12–18	46.09	13.51	3.67	36.23	33.86	93.4
	18–24	53.09	24.01	6.17	16.73	14.62	87.4
	24–30	65.15	19.91	5.47	9.47	5.41	57.2
Cayucos sandy clay loam	0–6	56.53	21.68	5.24	16.55	13.17	79.5
	6–12	53.38	22.07	4.38	20.17	16.63	82.6
	12–18	42.17	17.20	4.20	36.43	34.22	94.0
	18–24	52.91	13.96	3.35	29.78	27.59	92.7
	24–30	60.33	13.84	3.75	22.08	19.00	86.1
	30–36	63.46	16.86	3.26	16.42	13.80	84.1
Colma II sandy loam	0–6	62.34	21.55	4.90	11.21	9.32	83.0
	6–12	63.76	20.10	5.03	11.11	8.63	79.6
	12–18	62.03	22.28	4.10	11.59	9.89	85.4
	18–24	57.53	20.68	4.62	17.17	14.78	86.0
	24–30	59.58	21.45	3.11	15.86	14.60	92.1
	30–36	64.58	22.05	4.12	9.25	7.55	81.6
Colma I sandy loam	0–6	60.70	22.35	5.07	11.88	9.39	79.0
	6–12	60.36	22.32	4.44	12.88	10.33	80.4
	12–18	56.20	23.75	4.58	15.47	13.01	84.2

It may be noticed that the excess of bases over NH_4^+ adsorbed increases greatly with depth in the Sheridan profile; only slightly in the Sweeney profile; and not at all in the Colma II profile.

It is important to note that regardless of the excess of bases over NH_4^+ adsorbed, the pH of the Sheridan profile and of the surface horizons of the Sweeney profile is on the acid side. This fact leads us to the conclusion that the excess of bases over the NH_4^+ adsorbed is not due to soluble salts, but must be due to the treatment of the soils with NH_4-acetate. It

TABLE 4

Mechanical analysis of the California prairie soil colloids

SOIL COLLOID FROM	DEPTH	FRACTIONS		
		$<1\mu$	$<0.5\mu$	$<0.25\mu$
		Per cent of extracted sample	Per cent of $<1\mu$	Per cent of $<1\mu$
	inches			
Sweeney	0–6	91.16	78.29	51.90
	6–12	91.57	76.96	47.18
	12–18	94.18	85.06	57.61
	18–24	95.19	85.45	62.16
	24–30	88.61	76.03	46.07
	30–32	89.52	73.13	44.77
Sheridan	0–6	95.69	82.01	59.33
	6–12	96.34	88.17	65.15
	12–18	97.49	86.78	65.45
	18–24	99.50	89.05	72.71
	24–30	98.05	91.12	72.13
Cayucos	0–6	98.00	85.98	76.80
	6–12	97.61	91.16	82.03
	12–18	99.23	96.01	88.92
	18–24	98.52	92.14	84.54
	24–30	99.56	94.31	83.84
	30–36	99.52	93.96	79.47
Los Osos	0–6	97.90	91.82	83.39
	6–12	98.79	93.64	85.34
	12–18	98.98	93.42	85.12
	18–24	98.84	90.97	83.00
	24–30	98.62	81.26	62.39

has been shown by Kelley and Jenny (11) that the NH_4-exchange capacity of biotite is far less than the Mg^{++} released by the treatment with NH_4-acetate. This is particularly pronounced in the Sheridan profile, in which the amount of biotite increases greatly with depth. This, therefore, may account for the excess bases, particularly since the percentage of Mg^{++} also increases with depth and is only slightly higher than the excess bases over NH_4 adsorbed. This is also true for the Colma I profile.

The amounts and distribution with depth of exchangeable H^+—expressed as a per cent of the NH_4-capacity, and commonly known as per cent unsaturation—are similar to those reported by Rost *et al.* for Minnesota prairie soils (17). The distribution with depth of the

exchangeable H^+ has a diffusion pattern and may serve as one of the most important common properties for the prairie soils. It is, at present, under further investigation.

From table 7 it may be seen that if the sum of the percentage contribution of all the fractions $< 2\mu$ is used as a basis for distinguishing the profiles studied, two groups appear: (a) those in which throughout the profile these fractions contribute only a part of the exchange capacity, 33 to 75 per cent; namely, the Sweeney, Sheridan, and Gleason profiles; and (b) those in which the contribution of these fractions is predominant in the upper part of the

TABLE 5

Base-exchange properties of some California prairie soils

SOIL	DEPTH	NH₄-EX-CHANGE* CAPACITY	TOTAL BASES	BASES, AS PER CENT OF TOTAL BASES				EXCHANGE-ABLE H⁺, AS PER CENT OF NH₄-EX-CHANGE CAPACITY†	pH OF SOIL
				Ca⁺⁺	Mg⁺⁺	Na⁺	K⁺		
	inches	*m.e.*	*m.e.*						
Cayucos	0–6	20.20	14.39	60.8	35.2	1.94	2.06	28.8	5.65
	6–12	21.20	17.86	58.1	38.5	1.56	1.84	15.6	6.11
	12–18	35.51	31.20	55.3	41.0	2.37	1.33	12.1	6.30
	18–24	32.62	28.51	53.5	41.4	4.10	1.00	12.6	6.25
	24–30	25.60	23.13	53.4	40.2	5.05	1.35	9.7	6.33
	30–36	23.55	21.90	53.5	41.4	4.40	0.70	7.0	6.57
Los Osos	0–6	20.20	18.65	70.54	27.1	0.91	1.45	7.68	6.05
	6–12	24.00	22.59	72.0	25.7	1.15	1.15	5.88	6.30
	12–18	28.04	27.15	72.6	25.2	0.90	1.30	3.17	6.60
	18–24	23.40	23.48	71.0	25.3	2.17	1.53	0.34‡	7.15
	24–30	23.21	24.90	70.7	25.9	1.80	1.60	1.69‡	8.03
Colma I	0–6	17.15	14.97	53.2	39.9	3.20	3.70	12.70	6.50
	6–12	16.10	14.32	47.2	46.3	4.36	2.14	11.03	6.40
	12–18	17.87	16.15	30.8	60.5	7.00	1.70	9.64	6.10
Gleason	0–6	31.55	25.60	78.7	18.0	1.14	2.79	18.95	6.82
	6–12	31.79	25.84	77.7	17.8	1.48	3.20	18.72	6.66
	12–18	30.45	26.68	76.3	19.0	1.23	3.47	12.40	6.94
	18–24	35.20	33.13	76.1	20.1	1.00	2.80	5.88	6.95
	24–30	39.15	36.41	74.3	21.7	1.43	2.57	7.00	6.97
	30–36	38.40	35.22	74.5	21.8	1.30	2.40	8.28	6.87

* Base-exchange capacity determined by NH_4Ac is expressed as milliequivalents per 100 gm. of soil dried at 105° C.

† Exchangeable H^+ = NH_4-exchange capacity less total bases.

‡ Bases in excess of exchange capacity.

profile, 85 to 95 per cent, but not so in the lower part, in which it is only 50 to 60 per cent; namely the Los Osos and Cayucos profiles. This differentiation emphasizes the important contribution of the silt and sand fractions to the exchange capacity of the soil.

The NH_4-exchange capacities of the colloids from the different soil profiles and from the same profile vary considerably, but they have a positive correlation with the silica-alumina ratios; namely, the NH_4-exchange capacity is higher, the higher the silica-alumina ratio of the colloid (fig. 2).

Total chemical analyses of soils and colloids

Standard procedures were employed for the chemical analysis.

Complete chemical analyses of the whole soil were run on every horizon from four profiles, the Sweeney, Sheridan, Cayucos, and Los Osos (table 8).

Complete analyses were made on the colloids from every horizon of three profiles, the Sweeney, Sheridan, and Cayucos (table 9). Only partial chemical analyses were made on the colloids from the Los Osos, Gleason, and Colma II profiles (table 10).

TABLE 6

Base-exchange properties of some California prairie soils

SOIL	DEPTH	NH₄-EXCHANGE CAPACITY	TOTAL BASES	BASES, AS PER CENT OF TOTAL BASES				BASES IN EXCESS OF EXCHANGE CAPACITY IN PER CENT OF EXCHANGE CAPACITY	pH OF SOIL
				Ca^{++}	Mg^{++}	Na^+	K^+		
	inches	*m.e./100 gm.*	*m.e./100 gm.*						
	0–6	57.50	59.72	76.1	21.3	1.30	1.30	3.87	6.75
	6–12	59.50	61.28	73.04	25.2	1.19	0.57	3.00	6.85
Sweeney	12–18	61.15	64.01	75.7	22.6	1.27	0.43	4.68	6.95
	18–24	60.10	63.93	79.14	19.4	1.13	0.31	6.28	6.95
	24–30	57.50	51.41	82.1	16.1	1.34	0.46	....	7.15
	30–32	46.50	52.82	73.5	24.3	1.60	0.60	13.60	7.70
	0–6	23.88	21.52	67.6	27.9	1.73	2.77	9.92*	6.35
	6–12	22.65	23.42	66.9	30.3	1.68	1.12	3.40	6.30
Sheridan	12–18	21.34	23.99	61.3	35.2	2.30	1.20	12.41	6.35
	18–24	16.20	25.04	53.0	43.5	2.47	1.03	54.50	6.60
	24–30	13.20	22.36	49.4	46.9	2.66	1.04	69.50	6.85
	0–6	15.95	18.92	83.25	13.6	2.07	1.08	18.65	7.10
	6–12	15.85	18.88	85.5	12.7	1.05	0.75	19.12	7.50
Colma II	12–18	17.55	15.88	77.0	20.3	1.64	1.06	....	7.70
	18–24	18.71	22.20	68.6	28.3	1.59	1.51	19.05	7.80
	24–30	15.90†	.....	....	....	....	....	....	8.10

* Exchangeable H^+.
† Carbonates present.

The variation in chemical composition among the soils is very considerable and is, of course, a reflection of the difference in the mineralogical composition of the parent materials. The variation in chemical composition with depth in each profile is a reflection of the variation with depth in the rate of clay formation and of the redistribution of the clay due to migration. These variations are not unique to the prairie soils and therefore need not be discussed.

The most interesting observation of the chemical composition of the colloids is that their absolute silica-alumina ratios (tables 9 and 10) vary considerably between profiles, that is to say, they range between the limits of 3.32 and 7.26.

This variation is significant; it upsets the notion that prairie colloids possess a definite silica-alumina ratio within the limits of 3.14 and 4.68 as suggested by Caldwell and Rost (8). The wide limits of the California prairie colloids in contrast to the midwestern prairie colloids can be attributed to the variation in their parent material. Whereas many of the midwestern prairies have developed on relatively uniform parent materials, the California prairies have

TABLE 7

Percentage contribution of clay and silt + sand fraction to the NH_4-exchange capacity of California prarie soils

SOIL	DEPTH	NH_4-EXCHANGE CAPACITY OF WHOLE SOIL	CONTRIBUTION OF WHOLE CLAY $<2\mu$	CONTRIBUTION OF SAND + SILT
	inches	*m.e./100 gm.*	*per cent*	*per cent*
Sweeney	6–12	59.50	54.2	45.8
	18–24	60.10	57.1	42.9
	30–32	46.50	33.9	66.1
Sheridan	0–6	23.80	63.4	36.6
	6–12	22.65	73.2	26.8
	18–24	16.20	60.0	40.0
	24–30	13.20	51.8	48.2
Gleason	0–6	31.55	57.1	42.9
	6–12	31.79	59.5	40.5
	12–18	30.45	63.8	36.2
	18–24	35.20	71.3	28.7
	30–36	38.40	57.7	42.3
Cayucos	0–6	20.20	71.8	28.2
	6–12	21.20	80.7	19.3
	12–18	35.51	87.9	12.1
	18–24	32.62	77.2	22.8
	24–30	25.60	71.6	28.4
	30–36	23.55	57.3	42.7
Los Osos	0–6	20.20	83.2	16.8
	6–12	24.00	87.5	12.5
	12–18	28.04	93.0	7.0
	18–24	23.40	56.5	43.5
	24–30	23.21	32.0	68.0

developed from a wide variety of parent material, as seen in table 1. Since the colloids develop from specific minerals, as will be discussed elsewhere, they reflect the nature of these minerals. Thus, the Sweeney colloid reflects the chemical composition of augite, whereas the Sheridan colloid reflects that of the mica of its parent material.

It is significant, however, that notwithstanding the great variations in the colloids from one profile to another, the nature of the variation in the composition

with depth of the colloids in each of the profiles is alike, and it is similar to colloids from the midwestern prairie soils. This variation with depth is best expressed by the relative values of silica-alumina ratios (*sa*), and iron-alumina ratios (*fa*) as plotted in figure 3. It may be seen that the lowest *sa* ratios are not at the surface but at the point in the profile which shows the greatest amount of clay accumulation or the highest proportion of the smaller clay fractions, such as in the Sweeney, Cayucos, and Los Osos (table 4). This indicates that the silica-alumina ratios of the clay fractions decrease with decreasing particle size. The common feature among the profiles with respect to the iron-alumina ratios is that the ratios increase with depth.
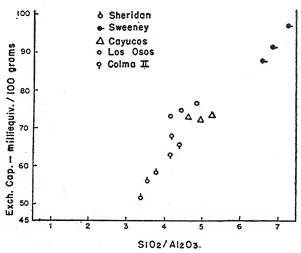

FIG. 2. RELATIONSHIP BETWEEN NH₄-EXCHANGE CAPACITY AND SILICA-ALUMINA
RATIO FOR THE INORGANIC CALIFORNIA PRAIRIE SOIL COLLOIDS

Differential thermal analyses of the colloids

Differential thermal analysis is useful in identifying the type of clay mineral present in a soil. It has been used for this purpose by several investigators who have shown that the release of water (which appears as endothermic breaks in the differential thermal curves) at a temperature above 200°C. takes place at a specific temperature which is characteristic for each mineral. The apparatus used in the analysis is described by Page (16).

The colloids, prior to the analysis, were treated with hydrogen peroxide to destroy the organic matter, then air-dried, and ground to pass through an 80-mesh screen. It was not deemed necessary to bring the samples to an equilibrium with some given relative humidity prior to the analysis, for it was felt that the first endothermic peak which this treatment might affect, is no aid in the identification of clay minerals.

The results of these analyses are recorded in figures 4 and 5. Analyses were also run on extracted mica from the Sheridan profile.

From these figures, it is possible to make the following observations:

All the colloid samples show an endothermic break at low temperatures, ranging between the starting temperature, 20°, and about 200°C. This break represents the loss of the adsorbed water. Its depth and width depend on several factors: (a) the relative humidity at

TABLE 8

Chemical composition of some California prarie soils

In percentages of weight of soil after ignition

SOIL	DEPTH	SiO₂	TiO₂	Fe₂O₃	Al₂O₃	MnO	CaO	MgO	K₂O	Na₂O	P₂O₅	TOTAL	H₂O + 105°C. (COMBINED)
	inches												
Sweeney	0–6	52.34	1.64	15.07	11.00	0.09	8.47	10.55	0.45	1.53	0.18	101.32	6.16
	6–12	51.90	1.99	14.51	10.95	0.07	8.24	10.18	0.20	1.41	0.17	99.62	6.76
	12–18	51.85	1.85	15.12	11.90	0.08	8.14	10.48	0.32	1.20	0.16	100.79	7.14
	18–24	51.70	1.83	14.71	11.86	0.07	8.11	10.39	0.23	1.45	0.16	100.51	6.70
	24–30	51.49	1.97	15.42	11.11	0.07	7.84	9.56	0.34	2.06	0.13	99.99	6.28
	30–32	51.88	1.89	15.45	12.65	0.11	7.39	6.69	0.64	3.06	0.14	99.90	2.31
Sheridan	0–6	62.48	0.99	9.99	16.29	0.06	3.98	1.59	0.30	3.02	0.19	98.89	4.52
	6–12	60.56	1.01	10.56	17.23	0.06	3.60	1.85	0.29	2.59	0.17	98.15	4.20
	12–18	62.51	1.13	10.34	15.25	0.07	3.42	1.54	0.43	3.82	0.52	99.03	4.21
	18–24	56.90	1.49	16.28	14.04	0.07	4.56	2.60	0.88	3.48	0.18	100.48	5.10
	24–30	54.29	1.73	17.93	14.12	0.07	5.15	2.99	0.52	2.89	0.22	99.91	4.95
Cayucos	0–6	75.65	0.56	3.31	12.58	Tr	2.51	0.71	1.28	2.23	0.25	99.08	1.14
	6–12	75.21	0.55	3.23	13.64	Tr	2.56	0.78	1.43	2.37	0.25	100.02	1.89
	12–18	70.91	0.63	5.15	15.71	Tr	2.51	1.28	1.54	2.31	0.25	100.29	2.14
	18–24	70.71	0.57	4.88	15.80	Tr	2.65	1.24	1.18	1.69	0.25	98.97	2.60
	24–30	71.22	0.53	4.25	15.32	Tr	2.97	1.14	1.06	1.70	0.25	98.44	2.01
	30–36	70.57	0.57	4.41	15.55	Tr	3.15	1.24	1.38	2.47	0.24	99.58	1.85
Los Osos	0–6	72.68	0.58	5.22	13.99	N.D.	3.33	1.33	2.87*		......	100.00	2.13
	6–12	72.10	0.58	5.34	14.45	N.D.	3.15	1.50	2.88*		......	100.00	3.07
	12–18	71.28	0.56	5.80	15.24	N.D.	2.99	1.65	2.48*		......	100.00	3.48
	18–24	72.86	0.52	5.05	14.15	N.D.	3.06	1.56	2.80*		......	100.00	2.85
	24–30	72.26	0.52	5.25	14.42	N.D.	3.16	1.72	2.67*		......	100.00	3.45

* By difference.

which the sample was dried; (b) the percentages of the different particle sizes in the sample < 1μ clay, for the greater the proportion of smaller particles, the greater will be the adsorbed water; (c) the chemical compositoin—at least the nature of the exchangeable ions and their amounts; (d) the state of aggregation of the colloidal particles, since it, too, affects the amount of adsorbed water.

The second endothermal breaks for the colloids from the Sheridan, Gleason, Los Osos, and Cayucos, and for the extracted mica from the Sheridan, occur at about the same range of temperature, namely between 500° and 550°C (fig. 4). The depth and the width of the

break in the Sheridan samples increase with decrease in particle size, that is, $< 1\mu > (5\text{-}50\mu)$ $> (50\text{-}100\mu)$. This change is brought about not merely by the decrease in the particle size, but also by an increase in the combined water, which takes place during the breakdown of the mica to colloidal fractions. The similarity between the curves of the mica and the soil colloids leads to the conclusion that the soil colloids are of the hydrous mica-like clay minerals. These differential thermal curves are also similar to several midwestern prairie colloids reported by Russell and Haddock (18).

In figure 5 it may be seen: (a) that the differential thermal curves of the Sweeney colloids are very similar to that of a vermiculite from Libby, Montana. This vermiculite, however, is not, according to Gruner (9), a true vermiculite but a hydrobiotite—a mineral which con-

TABLE 9

Chemical composition of some California prairie colloids

In percentages of weight of colloid after ignition

SOIL COLLOID FROM	DEPTH	SiO_2	TiO_2	Fe_2O_3	Al_2O_3	MnO	CaO	MgO	K_2O	Na_2O	P_2O_5	TOTAL	$H_2O +$ 105°C. (COMBINED)	$\frac{SiO_2}{Al_2O_3}$
	inches													
	0–6	47.00	1.41	18.08	11.76	0.11	6.39	11.73	0.91	1.38	0.18	98.95	......	6.78
	6–12	48.00	1.41	18.05	12.49	0.12	6.34	12.00	0.56	1.15	0.22	100.94	11.72	6.54
Sweeney	12–18	47.95	1.40	18.80	12.69	0.08	5.96	12.17	0.66	1.57	0.24	101.52	......	6.41
	18–24	47.43	1.41	18.78	11.77	0.11	5.82	11.97	0.71	1.57	0.37	99.94	11.01	6.85
	24–30	47.73	1.40	19.80	12.15	0.14	5.45	11.99	0.70	1.31	0.17	100.84	......	6.66
	30–32	47.08	1.38	25.27	11.01	0.17	4.17	9.91	0.50	1.44	0.13	101.06	9.60	7.26
	0–6	45.56	2.02	22.65	22.25	0.12	2.66	3.18	0.86	0.55	0.55	100.40	16.64	3.47
	6–12	45.29	2.02	23.02	22.50	0.11	2.65	3.48	0.98	0.57	0.39	101.01	16.17	3.41.
Sheridan	12–18	45.15	1.99	23.44	23.07	0.08	2.47	3.36	0.81	0.54	0.43	101.34	......	3.32
	18–24	46.62	2.56	23.36	22.36	0.05	1.98	2.85	0.68	0.33	0.33	101.12	15.15	3.54
	24–30	46.65	2.51	23.47	20.94	0.08	1.98	2.66	0.83	0.43	0.28	99.83	14.58	3.78
	0–6	61.17	0.83	10.78	21.08	0.03	3.43	2.32	0.66	0.82	0.20	101.32	9.94	4.93
	6–12	59.72	0.76	10.61	21.12	0.01	5.10	2.39	0.59	0.29	0.18	100.77	......	4.79
Cayucos	12–18	59.13	0.74	11.33	21.64	0.01	5.63	2.54	0.61	1.24	0.11	102.98	......	4.63
	18–24	58.52	0.76	11.23	20.06	0.01	6.89	2.63	0.75	1.19	0.12	102.16	13.62	4.94
	24–30	60.41	1.14	11.71	20.04	0.01	4.22	2.98	0.47	0.92	0.13	102.03	......	5.12
	30–36	58.69	0.68	11.41	19.03	0.01	7.58	3.14	0.94	1.10	0.15	102.73	13.40	5.25

sists of alternating sheets of vermiculite and biotite. This is confirmed by the two endothermal breaks in the higher temperature range; the one between 500° and 550°C. although small, corresponds to the one in hydrous mica; and the one between 800° and 850°C. corresponds with the one in a magnesium-bearing mineral such as talc (16); and (b) that in the Colma II profile, the colloid from the 30-36-inch horizon has a differential thermal curve which is similar to that of the vermiculite, whereas the colloids from 6 to 12 inches has a differential thermal curve similar to that of a bentonite (16).

In several of the colloids, there is an exothermic break ranging between 450° and 470°C. It is most conspicuous in the colloid from Colma II, and to a smaller degree in the colloids from Sheridan, Gleason, and the Sweeney profiles. This break corresponds with a similar break which occurs in the differential thermal curve of freshly prepared $Fe(OH)_3$ (fig. 5.) This similarity suggests the presence of free $Fe(OH)_3$ in these colloids.

Results of x-ray analyses

X-ray studies were made on some of the colloids from each of the profiles under investigation.

If the x-ray patterns did not change on heating, the pattern of the heated samples is not given; if only one spacing changed in the pattern, only the change of the spacing is recorded. The results of these samples are given in table 11.

TABLE 10

Chemical composition of some California prairie colloids

In percentages of weight of colloid after ignition

SOIL COLLOID FROM	DEPTH	SiO_2	TiO_2	Fe_2O_3	Al_2O_3	$CaO + MgO + Na_2O + K_2O*$	TOTAL	$H_2O + 105°C.$ (COMBINED)	$\frac{SiO_2}{Al_2O_3}$	CO_2 FROM CARBONATES
	inches									
	0–6	56.4	0.57	11.00	25.40	6.63	100.00	....	3.77	....
	6–12	56.4	0.57	11.17	27.01	4.85	100.00	13.73	3.54	....
	12–18	56.2	0.57	11.20	27.30	4.73	100.00	15.30	3.50	....
Gleason	18–24	56.7	0.56	11.45	27.39	3.90	100.00	14.77	3.52	....
	24–30	56.5	0.47	11.20	27.55	4.28	100.00	....	3.49	....
	30–36	56.5	0.41	12.10	26.79	4.20	100.00	14.32	3.59	....
	0–6	57.3	0.74	12.67	23.30	5.99	100.00	12.90	4.18	....
	6–12	57.3	0.73	12.71	23.16	6.10	100.00	....	4.22	....
Los Osos	12–18	58.5	0.72	12.41	22.45	5.92	100.00	11.20	4.43	....
	18–24	58.2	0.73	13.17	21.90	6.00	100.00	....	4.52	....
	24–30	59.3	0.70	12.72	20.75	6.53	100.00	12.05	4.86	....
	0–6	52.65	0.73	10.12	21.50	15.00	100.00	14.10	4.16	.....
	6–12	52.75	0.77	10.11	21.00	15.37	100.00	.....	4.27	.....
Colma II	12–18	52.01	0.65	9.03	21.25	17.06	100.00	12.50	4.16	.....
	18–24	51.85	0.64	8.34	21.00	18.17	100.00	13.50	4.19	.....
	24–30	39.19	0.53	7.69	16.19	36.40	100.00	13.00	4.12	16.00
	30–36	21.12	0.24	7.70	8.16	62.78	100.00	12.80	4.40	38.75

* By difference.

The following observations may be made from the x-ray analysis:

The diffraction patterns of all the colloids are identical to that of muscovite, with the following exceptions: (*a*) the Colma II, Los Osos, and Sweeney colloids have the montmorillonite spacings in the unheated samples. (*b*) On heating, with the exception of the Sweeney colloids, the change in the pattern occurs in only one spacing, namely, in the Colma this spacing shifts from 14.47 to 10.00 A. A similar shift occurs in the Los Osos, but the spacing of the 0–6-inch sample is weak and is not so clearly defined. In the Cayucos, Gleason, and Sheridan no shifting occurs, but the 10 A. spacing either appears like that in the 0–6-inch samples of the Cayucos and Gleason or becomes more distinct, as in the 30–36-inch sample of the Cayucos and Gleason and in both of the Sheridan samples. (*c*) The Sweeney x-ray pattern on heating becomes identical with that of talc. This involves changes in the following spacings: The 14.47 A. spacing shifts to 9.65 A., the 2.60 A. spacing appears in the heated sample whereas it is absent in the unheated, the 2.56 A. spacing shifts to 2.50 A.
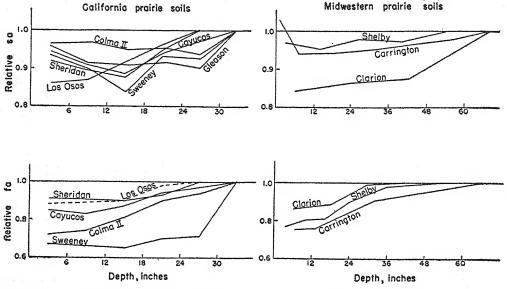
FIG. 3. RELATIONSHIP BETWEEN RELATIVE SILICA-ALUMINA RATIO (*sa*) AND RELATIVE IRON-ALUMINA RATIO (*fa*), AND DEPTH FOR SEVERAL CALIFORNIA AND MIDWESTERN PRAIRIE COLLOIDS

TABLE 11

Effect of partial dehydration* on interplanar spacings of California prairie colloids

TEMPERA-TURE	SHERIDAN		CAYUCOS		LOS OSOS	
	0–6 inches	24–30 inches	0–6 inches	30–36 inches	0–6 inches	30–36 inches
°C.	A.	A.	A.	A.	A.	A.
25°	10.34 w.†	10.27 v.w.	no spacing	10.13 v.v.w.	14.33 w.	14.33 m.
600°	10.20 m.	10.20 w.	9.95 w.	9.95 w.	9.90 m.	10.13 m.

TEMPERA-TURE	GLEASON		COLMA II		SWEENEY		
	0–6 inches	30–36 inches	0–6 inches	30–36 inches	18–24 inches		
°C.	A.	A.	A.	A.	A.	A.	A.
25°	no spacing	no spacing	14.47 m.s.	10.27 v.w.	14.47 s.....	....	2.56 m.s.....
600°	10.20 v.v.w.	10.27 v.v.w.	10.00 m.	10.06 m.	9.65 m.....	2.60 s.....	2.50 s.....

* The position and intensities of the other lines are not affected by dehydration.

† Symbols for intensities of x-ray reflections: s. = strong; m.s. = medium strong; m. = medium; m.w. = medium to weak; w. = weak; v.w. = very weak; v.v.w. = very, very weak.
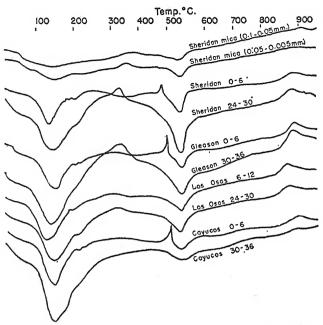
FIG. 4. DIFFERENTIAL THERMAL CURVES FOR SOME CALIFORNIA PRAIRIE COLLOIDS AND FOR MICA EXTRACTED FROM THE SHERIDAN SOIL
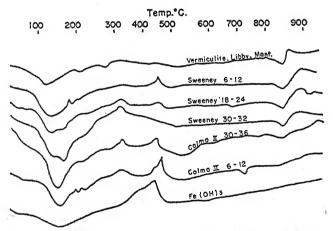

FIG. 5. DIFFERENTIAL THERMAL CURVES FOR SOME CALIFORNIA PRAIRIE COLLOIDS, (VERMICULITE (LIBBY, MONTANA), AND FOR FRESHLY PREPARED Fe(OH)₃ (DRIED FIRST AT 100°C. AND THEN COOLED IN THE AIR BEFORE RUNNING OF SAMPLE)

These three spacings, the 9.65, 2.60, and 2.48 A. (or 2.50 A.), particularly when their intensities are taken into consideration, are the spacings which distinguish talc from muscovite. According to Gruner (9) this property of assuming the talc pattern on heating is characteristic of the vermiculites.

The x-ray data have corroborated the findings of the differential thermal analysis, namely, (a) that the colloids from the Cayucos, Gleason, and Sheridan profiles are mica-like clay minerals, which have been called by several names such as "sericite," "illite," and "hydrous mica"; (b) that the colloids from the upper horizons of Colma II are montmorillonitic in nature; (c) that the Los Osos has an x-ray pattern of montmorillonitic clay but a differential thermal curve of hydrous mica clay; and (d) that the Sweeney colloids consist mainly of Gruner's hydrobiotite, a clay mineral with an expanding lattice-like montmorillonite, but which is made up of alternating sheets of vermiculite and hydrous mica. This conclusion is also supported by the chemical composition of these colloids (table 9); it is similar to the composition of Gruner's hydrobiotites. It is believed that this clay mineral type is reported, for the first time, to be the main constituent of a soil colloid.

SUMMARY AND CONCLUSIONS

From the results presented it is possible to conclude that the so-called California prairie soils are indeed as true prairie soils as those of the Midwest. It is also possible to define the prairie soils more precisely than in the past, and the definition may be based on those soil properties which show only a small variation between profiles. These are, besides dark brown to black surface color, granular structure, and absence of lime accumulation in the profile, the predominance of Ca and Mg ions among the exchangeable bases, the presence of exchangeable H^+ throughout the profile, the three-layer type of the crystal lattice of the clay minerals, the nature of the correlation with depth—a diffusion pattern—of the pH, of the percentage unsaturation, of the C, of the N, and of the C/N ratio, and also the nature of the variation with depth in the composition of the clay. The common feature with respect to the clay distribution with depth is that the pattern of the distribution is a result of extensive clay migration. Even in profiles like the Sheridan and Marshall, where there is no increase in percentage of clay with depth but rather a constant percentage down to about 20 inches and a gradual decrease below this depth, clay migration must have been extensive. This conclusion is arrived at as follows: since the rate of clay formation decreases with depth it will be expected that if no clay migration has taken place, the pattern of the distribution with depth of the clay should be a gradual decrease from the surface downward. Therefore, a pattern of distribution such as that of the Sheridan and the Marshall can be obtained only through a redistribution of the clay through migration downward.

The prairie soil profiles, however, have properties in which they show large variations. These variations are in the chemical composition of the whole soil and colloid, in the mineralogical composition of the whole soil, and in the mechanical analysis of the soils.

An examination of the like properties of the prairie soil profiles reveals that these are primarily the result of the common soil-forming factors, namely, climate, vegetation, and relief, whereas the unlike properties are the result of the unlike soil-forming factor, namely, parent material. It is quite obvious, therefore, that if it is desirable to compare soils under moderate weathering conditions, they can be compared only by properties that are chiefly the result of the climate, vegetation, and relief, namely, organic matter, exchangeable

hydrogen, and the variation with depth of the pH, chemical composition of the clay, and lime distribution. The great soil groups under such weathering conditions as the prairies, the chernozems, the chestnuts, etc., can be based, therefore, only on a few properties, and it is necessary to remember that these soil groups do not imply that the soils in any one group are alike in other properties than the ones by which they were defined.

If this definition of the great soil groups be accepted, then we have to accept the notion that the soil-forming factors do not play an equal role in the formation of a soil profile and that one or more factors may be the dominant influence in bringing about the common features among the soils of one great soil group.

It was shown that the California prairie soils and the midwestern prairie soils are very much alike in many soil properties, notwithstanding the fact that the soil-forming factors are not identical. The similarity of the soils, however, suggests that certain properties of the soil-forming factors of the two geographic regions must be alike, and dominant in determining certain soil properties. A careful evaluation of the soil-forming factors of the two regions leads to the conclusion that the dominant properties among the soil-forming factors for the prairies investigated are (a) climate—the climate as evaluated by Thornthwaite (20)—for both regions was evaluated as subhumid; (b) organisms—a dense ground cover of either grass or shrubs; (c) topography—upland with good drainage conditions; (d) time or age—fairly advanced (a considerable range for the midwestern prairies); (e) parent material—the one dominant property is the relatively high calcium and magnesium content (4.4–13.1 per cent).

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CHEMICAL RELATIONSHIPS OF POTASSIUM AND MAGNESIUM IN ORGANIC AND SANDY SOILS OF CENTRAL FLORIDA

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Most of the citrus groves of central Florida are planted on the sandy ridges because these are warmer and less susceptible to cold injury than the lower-lying surrounding areas. The soils on the ridges are light and relatively infertile. A surface soil sample will ordinarily show by analysis an exchange capacity of about 2 m.e., per 100 gm., and a subsoil sample about 1 m.e. Because of the high rainfall and the low inherent capacity of these soils to retain nutrients against leaching, citrus groves on the ridge soils are usually fertilized three times a year. It is of practical importance that these soils should be so managed as to ensure maximum retention of nutrient bases in forms available to citrus. There is some evidence from field studies that more magnesium is retained in the sandy ridge soils at relatively high than at low pH values. However, samples taken at the Citrus Experiment Station over a period of years indicate no clear-cut relationship of soil pH to potassium retention. This may be due partly to variations in the soil and partly to the fact that samples were taken but once or twice a year. The effects of soluble salts, basic residues, and hydrolysis on retention were not followed closely because of the infrequent sampling. The studies reported here were made in an effort to isolate these effects and obtain further information on the relationship of soil pH to the retention of potassium and magnesium in exchangeable forms in the soil.

EXPERIMENTAL METHODS

The mechanical composition of a representative ridge sandy soil, Norfolk fine sand, was determined. An oven-dried sample of soil was moistened with 30 per cent H_2O_2 and oven-dried at 70°C. repeatedly until there was no further loss in weight. The percentage loss was calculated and was tabulated as "organic matter." The treated sample was separated into size fractions by sifting in a nest of sieves with openings varying from 1 to 0.05 mm. in diameter. The soil material passing the smallest sieve was theoretically fractionated by suspending it in water and taking samples at fixed depths below the surface of the suspension at suitable time intervals as calculated by Stoke's law for settling velocities. The percentage of each size fraction was calculated on the basis of the oven-dried weight of the whole soil. The exchange capacity of an untreated sample and also of a sample treated with H_2O_2 was determined from the quantity of ammonium found absorbed from neutral normal ammonium acetate after the excess salt was removed by washing with neutral 80 per cent ethyl alcohol.

Hydrated lime, when CO_2 is excluded, can be expected to react completely

[1] Contribution from the Citrus Experiment Station, Lake Alfred, Florida.

with an acid soil, the end products being exchangeable calcium and water. On
the other hand, both dolomite and ground limestone when applied in large
quantities leave unreacted residues for long periods. Experiments were made
to determine what effect these residues would have on potassium and magnesium
adsorption from fertilizer salts. Three soils were used—Norfolk fine sand,
Blanton fine sand, and a muck. Equal portions of a well-mixed bulk soil sample
were weighed into a series of flasks and a series of beakers. Varying amounts
of calcium carbonate were added to the beakers and varying amounts of calcium
hydroxide to the flasks. Equal portions of a dilute solution of magnesium
sulfate and potassium chloride were added to the two series. The solution
was made so as to give an equivalent ratio of 4:1 for K_2O to MgO. The amount
of salts added to each soil sample corresponded to that which the soil would
receive in one ordinary application of fertilizer. The flasks were stoppered
and shaken and the beakers stirred frequently for 1 hour. Portions of the
suspensions were taken for pH determinations. The remainder of each sus-
pension was allowed to settle another hour and then aliquots of the clear solu-
tions were analyzed for magnesium and potassium.

   To test the effect of hydrolysis on potassium and magnesium retention,
Norfolk fine sand was used. A bulk sample was H-saturated by leaching it
with a large volume of $0.01\ N$ HCl and washing it free of chloride with distilled
water. From this soil, potassium-, magnesium-, and calcium-saturated samples
were prepared by neutralizing portions of the bulk sample with KOH, $Mg(OH)_2$
and $Ca(OH)_2$. Soil suspensions with 50 gm. of K-saturated soil and varying
amounts of Ca-saturated with H-saturated soil in 250 ml. distilled water were
mixed so as to give a constant amount of soil in each suspension but with pH
values from 5.2 to 7.0. An additional suspension of K-saturated soil with 100
mgm. $CaCO_3$ was prepared to check the effect of residual calcium carbonate on
the mobilization of potassium. Another series was prepared just like this
except that Mg-saturated instead of K-saturated soil was used. The suspen-
sions were shaken for 1 hour and filtered. To remove finely dispersed colloidal
material the filtrates were frozen, thawed, and filtered again. The clear solu-
tions were analyzed for potassium and magnesium.

   A soil-leaching experiment was designed and carried out to get some idea as
to how the effects of soil reaction on adsorption, cation exchange, and hydrolysis
fit together in a practical way. Different amounts of lime were added to moist
portions of a well-mixed sample of H-saturated Norfolk fine sand so as to give
a pH range of 3.5 to 7.3. After the soil had air-dried, 100-gm. samples were
weighed from each portion into large centrifuge bottles so as to give four series
covering the pH range. To each bottle in one series, 100 ml. of potassium
chloride solution containing 4 mgm. of K was added. The same amount of
this solution was added to another series, each member of which had received
20 mgm. of superphosphate. Since the effect of fertilizer salts is largely confined
to about the surface 6 inches of the sandy soils devoted to citrus in Florida,

this rate (400 pounds per acre-6-inches) is about the same as that ordinarily used in each of three applications per year in the field. In a manner similar to the potassium application, magnesium sulfate was added in solution so as to apply 1 mgm. of Mg to each of two series of samples, one of which had received superphosphate and one of which had not. The rates of additions of potassium and magnesium roughly corresponded to those ordinarily applied in the field. The bottles were shaken frequently for 1 hour and then centrifuged and 70 ml. distilled water was added. The shaking, centrifuging, and decanting process followed by the addition of water was repeated several times. Each of the extractants was analyzed for potassium and magnesium content.

Field experiments were also run to test the effect upon the retention of magnesium and potassium of "controlling" the pH between 5.5 and 6.0 with lime as compared with allowing the soil to remain acid (pH 4.7 to 5.1). Beginning

TABLE 1

Mechanical composition of a sample of Norfolk fine sand

	SIZE RANGE	PER CENT
Fine Gravel	(2–1 mm.)	0.2
Coarse Sand	(1–0.4 mm.)	10.5
Medium Sand	(0.4–0.25 mm.)	26.7
Fine Sand	(0.25–0.10 mm.)	60.1
Very Fine Sand	(0.10–0.05 mm.)	0.4
Coarse Silt	(0.05–0.01 mm.)	0.5
Fine Silt	(0.01–0.005 mm.)	0.1
Coarse Clay	(0.005–0.001 mm.)	0.3
Colloidal Clay	(0.001 mm. and smaller)	0.3
Organic Matter	....	0.8

in the spring of 1938, soluble magnesium, at the rate of 4 per cent MgO, and 8 per cent K_2O have been applied in 1,000 pounds of mixed fertilizer per acre three times a year to the soil in duplicate acid and limed plots in a block of magnesium-deficient grapefruit trees. Two check plots received the same fertilizer except that no magnesium was added. Composite soil samples were made by mixing 0–6-inch-deep cores taken in duplicate plots in January or February just before "spring" fertilization each year. These were analyzed for pH by means of a 1:1 soil-water suspension and the glass electrode and for exchangeable bases extracted with neutral normal ammonium acetate.

EXPERIMENTAL RESULTS

The mechanical composition of the Norfolk fine sand used in part of these experiments is shown in table 1. It is noteworthy that the bulk of the soil material is composed of coarse, medium, and fine sand. More than half of the colloidal material (by weight) is organic matter. The exchange capacity of the whole soil was found to be 2.02 and that of the soil treated with H_2O_2 to

be 0.38 m.e. per 100 gm., a loss of 1.64 m.e. due to the destruction of the organic matter.

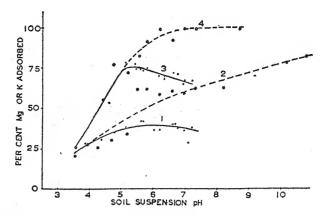Since the results of adsorption of potassium and magnesium from fertilizer

Fig. 1. Effect of pH and Carbonate Residues in Soil Suspensions on Adsorption of Magnesium and Potassium

Per cent of potassium applied in solution adsorbed in the presence of, 1, calcium carbonate and, 2, calcium hydroxide; similarly, per cent of magnesium adsorbed in the presence of, 3, calcium carbonate and, 4, calcium hydroxide.

TABLE 2

Relationship of soil reaction of Norfolk fine sand to release of adsorbed potassium or magnesium by hydrolysis

K-SATURATED SOIL	Mg-SATURATED SOIL	Ca-SATURATED SOIL	H-SATURATED SOIL	SOIL SUSPENSION	ADSORBED K OR Mg RELEASED*
gm.	gm.	gm.	gm.	pH	per cent
50	..	0	200	5.21	10.5
50	..	50	150	5.60	10.9
50	..	100	100	6.10	12.0
50	..	150	50	6.45	12.2
50	..	200	0	6.98	17.6
50	..	(100 mgm. CaCO₃)		8.40	50.3
..	50	0	200	5.15	2.54
..	50	50	150	5.58	4.54
..	50	100	100	6.05	4.75
..	50	150	50	6.50	4.87
..	50	200	0	6.95	5.33
..	50	(100 mgm. CaCO₃)		8.30	22.1

* From soil containing 2 m.e. of adsorbed K or Mg per 100 gm.

salts were similar for Norfolk fine sand, Blanton fine sand, and the muck used, only those for the Norfolk soil are reported. As shown in figure 1, the potassium adsorption by the samples receiving the hydroxide increased as the pH

increased, even to a very high pH, but in those receiving carbonate it increased only until a pH of 5.5 was reached, after which it fell off as the pH increased further. Similar results were obtained for magnesium adsorption, except that in the case of calcium hydroxide virtually all of the magnesium added had been
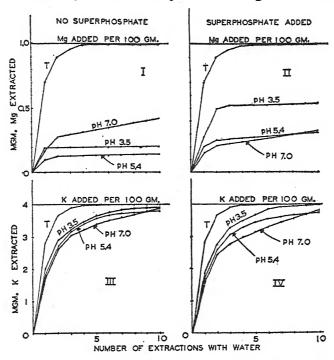

FIG. 2. EFFECT OF ADJUSTING H-SATURATED NORFOLK FINE SAND TO DIFFERENT pH LEVELS WITH LIME UPON THE LEACHING OF MAGNESIUM AND POTASSIUM IN THE ABSENCE AND THE PRESENCE OF SUPERPHOSPHATE

I—Milligrams of Mg extracted by water after addition of 1 mgm. Mg as sulfate to 100 gm. soil in absence of superphosphate.

II—Same as I except 20 mgm. superphosphate added to 100 gm. soil.

III—Milligrams of K extracted by water after addition of 4 mgm. K as chloride to 100 gm. soil in absence of superphosphate.

IV—Same as III except 20 mgm. superphosphate added to 100 gm. soil

In each case, the curve T indicates the theoretical rate at which free ions, unaffected by absorption or exchange processes, would be removed by dilution and extraction.

absorbed at pH 7.0. Similar results were found where the carbonate series was aerated with CO_2 at the level present in the air.

Increasing amounts of potassium and magnesium were released by hydrolysis in the absence of fertilizer salts (table 2) from Norfolk fine sand as the pH increased. Over the whole pH range studied, the release of potassium was about three or four times as great as that of magnesium. Also excess calcium carbonate was somewhat more effective in mobilizing potassium than magnesium.

The results of the soil leaching experiment are summarized in figure 2. Although the effects of soil reaction at eight different pH values between 3.5 and

TABLE 3

pH and exchangeable potassium* in soil samples taken† from an experimental block of citrus in January or February just prior to spring fertilization

DESCRIPTION OF PLOTS‡	1/21/38 pH	1/21/38 Exch. K	2/13/39 pH	2/13/39 Exch. K	2/5/40 pH	2/5/40 Exch. K	1/8/41 pH	1/8/41 Exch. K
Dolomite applications in oranges								
Check	4.70	25	4.60	67	4.94	43	4.80	51
200	4.94	48	4.95	102	5.39	52	5.09	44
400	4.99	36	5.05	80	5.35	86	5.11	70
800	5.56	41	5.45	93	6.26	80	5.90	35
1600	5.70	47	5.75	76	6.46	64	5.69	44
3200	5.90	56	6.10	107	6.71	56	6.09	48
6400	6.31	45	6.30	99	6.86	59	6.44	36
Dolomite applications in grapefruit								
Check	4.85	37	4.82	129	5.09	105	4.90	58
200	4.85	27	4.99	131	5.45	109	5.00	56
400	5.06	39	5.20	139	5.35	126	5.10	67
800	5.39	39	5.54	182	6.01	97	5.75	52
1600	5.69	58	5.85	109	6.35	117	5.85	67
3200	5.80	50	5.96	118	6.60	89	6.15	97
6400	6.30	43	6.15	105	6.65	120	6.10	60
Lime applications in oranges								
Check	4.75	20	4.75	83	4.85	46	4.75	53
200	5.15	47	5.00	84	5.31	53	5.00	40
400	5.40	41	5.19	70	5.50	62	5.39	50
800	5.54	45	5.76	109	6.19	63	6.25	56
1600	6.24	40	6.29	109	6.86	56	6.55	48
3200	6.64	43	6.55	130	7.00	80	6.80	44
6400	6.74	56	6.74	96	7.05	84	6.86	64
Lime applications in grapefruit								
Check	4.84	..	4.72	155	5.01	91	4.95	74
200	5.20	..	5.16	112	5.46	79	5.50	70
400	5.19	20	5.25	98	5.66	119	5.60	54
800	5.79	44	5.55	145	6.15	79	6.15	53
1600	5.76	56	5.65	151	6.46	111	6.25	92
3200	6.41	47	6.54	93	6.91	85	6.70	80
6400	7.05	38	6.84	99	7.19	109	6.70	95

* Exchangeable potassium in pounds per acre-6-inches.

† Composites were made of 14 cores per plot taken from the surface 6-inch soil layer.

‡ All applications in pounds per acre.

7.3 were determined, the general trend of results is shown very well by the curves for pH 3.5, 5.4, and 7.0. The curve T indicates the theoretical rate at which

free ions, unaffected by the adsorption or exchange processes in the soil, would be removed through simple dilution and extraction. At the rates ordinarily used, magnesium is much more strongly retained than potassium, regardless of the pH or of other fertilizer salts present. Magnesium is removed most rapidly at first at a low pH with a slow rate of hydrolysis and mobilization by dispersion after most of the free salts are washed out.

The results of the analyses of soils taken from the field plots are shown in tables 3 and 5. The quantity of potassium found in the soil any year just before spring fertilization is more closely related to seasonal variations in rainfall and rate of application of potassium than to soil pH (see tables 3 and 4). On the other hand, there is a significant increase in the exchangeable magnesium

TABLE 4

Relationship of rainfall and rate of fertilizer application to average quantities of exchangeable potassium found in citrus plots over a period of 4 years

	1937–38	1938–39	1939–40	1940–41
Inches of Rainfall*...........................	5.99	1.81	4.58	4.59
Orange Plots:				
Fertilizer Applied†........................	560	840	840	700
Average Exchangeable....................				
K Found‡..............................	42	93	63	49
Grapefruit Plots:				
Fertilizer Applied†........................	840	1260	1260	1050
Average Exchangeable....................				
K Found‡..............................	42	93	63	49

* Total inches of rainfall recorded at the Citrus Experiment Station during the interval between the "fall fertilization" and soil sampling each year.

† Pounds of fertilizer containing potassium equivalent to 8 per cent K_2O applied per acre each fall about 3 months prior to sampling of the soil.

‡ Average of the values recorded for exchangeable potassium in table 3.

held in the plots limed to an intermediate pH as compared with the unlimed plots.

DISCUSSION

The sandy soils of the ridge section of central Florida are similar in some ways to typical sands and sandy loams of other regions, but in some of their important physical and chemical characteristics they closely resemble many organic soils of Florida. When these sandy soils are moist, they behave like most sands in being highly permeable to water, and except where there is an impermeable hardpan near the soil surface, they drain freely after a heavy rain. Ordinarily they retain no more than 5 to 10 per cent moisture a few minutes after having been saturated. On the other hand, when they are thoroughly dried, they wet with difficulty. This property is associated with the soil organic

matter (1). It becomes very pronounced in the "dry bodies" under citrus trees and seems to be related to a peculiar type of tree decline.

Except for a very low exchange capacity, the sandy ridge soils are like the clay mineral soils in their cation-exchange reactions. With regard to the ease of exchange of the principal cations, the lyotropic series seems to hold. Since the principal metallic cation, calcium, is more easily displaced from the colloids than is the hyrogen ion, other cations are adsorbed from salts more readily at a high soil pH than at a low one (2). As for the chemical fixation of potassium in nonexchangeable forms, the colloids in these sandy soils exhibit this property weakly, if at all. Kime (3) showed that potassium has not accumulated in Norfolk fine sand of experimental plots and that the total potassium very closely approximates the exchangeable potassium. Even when a total of 4,500 pounds of potassium per acre has been applied to one plot over a period of 15 years, the total found was only 130 pounds per acre. Fertilizer is usually applied to citrus on the ridge soils three times each year. The potassium content of these sandy soils is seldom more than the amount added in two applications.

The explanation of the peculiar properties of the sandy ridge soils lies in the fact that they contain about 99 per cent siliceous sand and silt and very little colloidal clay, but approximately 1 per cent organic matter (see table 1). If 200 m.e. per 100 gm. is taken as the exchange capacity of soil organic matter and 50 m.e. as that of colloidal clay, then the distribution of the exchange capacity of this soil would be 1.68 m.e. due to organic matter and 0.15 m.e. due to colloidal clay. By actual analysis, the exchange capacity of the whole soil was 2.02 m.e. Furthermore, the destruction of the organic matter with H_2O_2 reduced the exchange capacity to 0.38 m.e. This verifies the general relationship Peech (4, 5) found between the exchange capacity and the organic matter content of the sandy soils of this group (an increase of 2 m.e. per 100 gm. per unit increase in percentage of organic matter). The exchange properties, the difficultly wettable condition, and the failure to fix potassium may be attributed to the organic nature of these soils. They may be thought of as organic sandy soils.

It is apparent from the absorption experiments reported that nutrient cations should be conserved by raising the pH of the sandy soils of central Florida to about 5.5 or 6.0. Care should be taken, however, not to use excessive amounts of lime. In practice, where CO_2 is not excluded, and because of the lack of intimate mixing, excess hydroxide would tend to revert to the carbonate before it completely reacted with the soil. Hence, there would be no advantage gained by excessive liming, regardless of the material used. The results of the experiment with calcium hydroxide show that the effect of soil pH on the adsorption of exchangeable cations from neutral salts by an organic soil or an organic sandy soil is similar to that reported by Peech and Bradfield (6) for a clay. That is, the higher the pH, the greater the adsorption. The results of the experiment in which calcium carbonate was used indicate that the excessive use of lime will result in a repression in adsorption of exchangeable cations from fertilizer salts over that which will result from adjusting the pH to about 5.5 to 6.0.

The repressive action of basic residues on the adsorption of potassium and magnesium can be attributed to the replacing effect of calcium ion. Although the solubility of calcium from the carbonate is very low, it is sufficient to affect the action of other cations furnished by soluble fertilizer salts in the soil solution. The effect should become pronounced when the CO_2 of the soil air is relatively high, and with continuous leaching, the calcium from the reservoir of basic residues would tend to replace and deplete other cations.

Peech and Bradfield (6) found that although a colloidal clay would adsorb more potassium from a neutral salt when the pH was increased, hydrolysis of the potassium from the clay was also more pronounced at higher than at lower pH values. This is in agreement with the results reported here (see table 2). As with colloidal clay, potassium and magnesium are more effectively adsorbed from neutral salts at a high pH than at a low one, but when the salts are leached from the soils the adsorbed potassium or magnesium is released by hydrolysis more rapidly at the higher pH values. It appears that colloidal clay and organic soil colloids are similar with regard to ordinary cation-exchange reactions, at least those involving hydrogen, calcium, magnesium, and potassium ions.

There may be some question as to whether a mixture of Ca-, K-, and H-saturated soils would behave in the same way as a soil having the same proportion of the various ions in the same soil complex. This objection is overcome, at least in part, by the results obtained in the leaching experiment. In this experiment either potassium or magnesium salt was added to soil samples having varying amounts of Ca and H in the complex. The results are in harmony with the adsorption and the hydrolysis experiments. The initial losses were most rapid with the soils of low pH, but later the effect tended to be reversed. This was especially true where magnesium was used. The greater rate of mobilization of magnesium, after the second extraction, at pH 7.0 over the rates found at lower pH values is due in part to the effect of more being left in the soil and may be partly attributed to the continued exchange reaction of slowly dissolving calcium from the unreacted lime residues and from increased mobilization by hydrolysis and dispersion with increased base saturation in these soils. It is quite clear that the initial losses of magnesium are high at low pH values but that the rate of mobilization subsequently is very low. In a practical way, where other salts are applied, it appears that there is better initial retention of magnesium from neutral salts at intermediate and high pH values than in strongly acidic soils. Magnesium will probably be sufficiently mobile and be best conserved at an intermediate pH value (about 5.5 to 6.0).

Potassium is extracted rapidly both in the presence and in the absence of other fertilizer salts. The adsorptive forces in the soil have no more than a feeble retarding effect on the removal of potassium, regardless of whether the pH is high, medium, or low. The loss, initially, is a little less at the higher pH values and in the presence of superphosphate. This may be due to decreased dispersion of colloidal material carrying adsorbed potassium by the action of calcium from superphosphate and residual lime. Hydrolysis of potassium appears to be a little lower at the lower pH values.

Even though soil solutions under growing conditions in the field are somewhat more concentrated than the extracting solutions used in the laboratory and ion replacement may be somewhat different under field and laboratory conditions, field data seem to be in general agreement with the laboratory results. Both indicate that soil reaction, within practical limits, is of little importance to the retention of potassium by light sandy soils (see figure 2 and table 3). The amount of potassium retained from fertilizer applications in the sandy soil of the ridge section of central Florida is determined largely by the amount and distribution of rainfall. From the laboratory results one might expect a slightly greater initial loss of potassium, other conditions being equal, at a low pH than at an intermediate or high pH and that the rate of mobilization and loss after

TABLE 5

pH and exchangeable magnesium* in soil samples taken from an experimental block of citrus in the winter months prior to spring fertilization

PLOT (BLOCK 9)	TREATMENT	SAMPLING DATES									
		11/19/39		1/29/41		2/10/42		2/3/43		3/6/44	
		pH	Ex. Mg	pH	Ex. Mg	pH	Ex. Mg	pH	Ex. Mg	pH	Ex. Mg
Plot 6	No lime, no Mg	5.00	11	5.20	14	4.81	12	5.00	15	5.00	12
Plot 7	No lime, no Mg	4.96	6	4.90	8	4.62	7	4.92	10	5.04	13
Plot 8	No lime, MgSO₄†	4.95	21	4.65	36	4.43	22	4.95	41	4.78	28
Plot 5	No lime, MgSO₄	4.85	18	4.95	33	4.71	29	4.80	42	4.85	29
Plot 9	Lime‡, MgSO₄	5.56	22	5.60	44	5.48	38	5.92	54	6.20	50
Plot 4	Lime, MgSO₄	5.80	22	5.80	48	5.70	44	6.10	73	6.10	45

* Pounds of exchangeable magnesium per acre-6-inches found in the composite samples of the surface 6-inch soil layer.

† The magnesium sulfate was mixed at the rate of 4 per cent MgO and applied in fertilizer three times a year at the rate of 1000 pounds per acre.

‡ Calcium carbonate applied in quantities intended to keep the soil pH in the approximate range of 5.5 to 6.0.

the washing out of soluble salts would be greatest at a high pH in the presence of unreacted lime. This point has not yet been verified by field data.

Accumulations of potassium in the sandy soils of central Florida are temporary and occur only where applications are made during droughts. With the occurrence of rainfall the potassium leaches (3). On the other hand, exchangeable magnesium seems to accumulate in light sandy soils of intermediate reaction (see table 5). No field data are available for the effect of excessive lime on the retention of magnesium, but one should expect, from the laboratory results reported here, that the tendency of the magnesium to accumulate would be less at pH 7.0 than at 5.5.

From the practical viewpoint, probably little is gained or lost in the conservation of potassium in, or added to, sandy ridge soils of Florida either by moderate or excessive liming. Much is doubtless gained in the conservation of magnesium through the careful application of lime or dolomite so as to result

in an intermediate soil reaction (pH 5.5 to 6.0). Because of the great importance of magnesium as a fertilizer material in the citrus industry of Florida, this is highly significant.
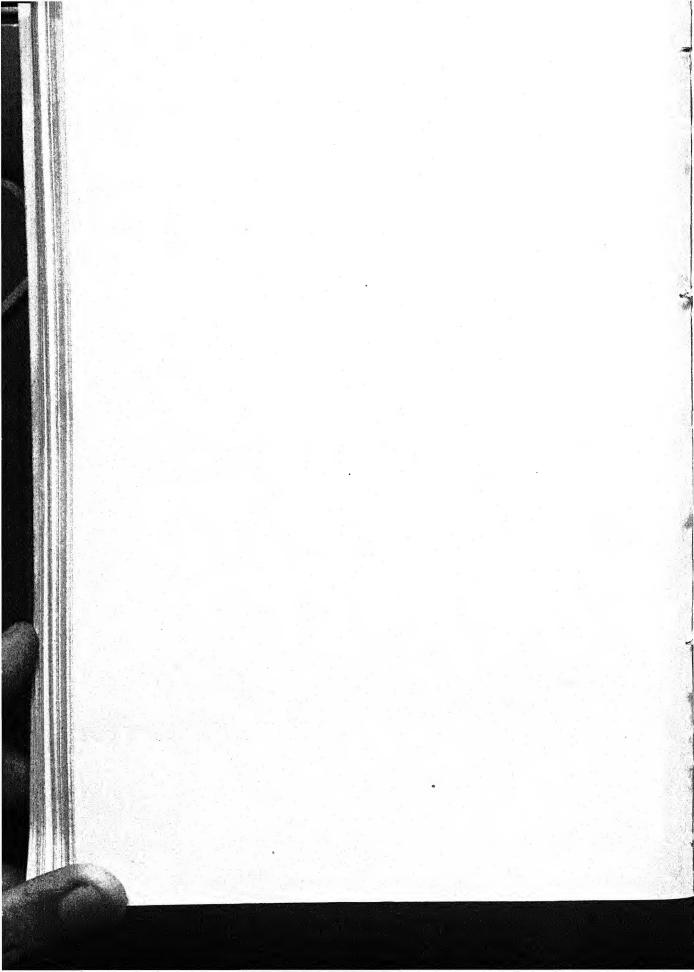
CONCLUSIONS

The light sandy soils of central Florida are essentially organic in their chemical reactions. The organic soils of Florida and the light sandy soils of the central ridge section are similar to ordinary clay mineral soils in that potassium and magnesium are more strongly adsorbed from neutral salts at high pH values than at intermediate or low values in the absence of unreacted lime residues, but in the presence of lime residues the retention is less at higher pH values than at an intermediate soil reaction. The effect of pH on the hydrolysis of adsorbed magnesium and potassium from organic and sandy soils is similar to that reported elsewhere for clay. The higher the pH, as controlled by increasing the proportions of exchangeable calcium, the greater the hydrolysis. Thus for the clays, sands, and organic soils that have been studied, loss of magnesium and potassium applied as neutral salts is greatest at low soil reactions until the salts are leached. Hydrolysis and mobilization of the remaining adsorbed magnesium and potassium are most rapid at high soil reactions and more rapid at an intermediate than at a low reaction.

Although the pH is a factor in the retention of potassium in light sandy and organic soils of Florida, potassium retention in these soils is so weak as to make pH of little practical consequence. On the other hand, magnesium is more strongly adsorbed, and the pH of the soil and the presence of unreacted lime residues are of great significance in magnesium conservation.

The light sandy and organic soils studied are dissimilar to clays in that they do not "fix" potassium in nonexchangeable forms—at least to any practical extent. The total potassium found in representative samples of light sandy soils of Florida is about the same as the sum of the soluble and exchangeable potassium. Potassium accumulates from applications only temporarily when there are droughty periods. When the rains come again, that which has accumulated is leached.

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OCCURRENCE OF SELENIUM IN PLEISTOCENE DEPOSITS AND THEIR DERIVATIVES IN SOUTH DAKOTA[1]

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Considerable interest in the occurrence and distribution of selenium has been aroused since the discovery that this element is the cause of "alkali disease." The distribution of selenium in Cretaceous formations has been investigated in South Dakota (6, 7, 8) and in other states (2, 5), and the occurrence in other geologic systems has been given some study (1, 5, 6, 8). Little information, however, has been available on the occurrence of selenium in Pleistocene deposits (3, 12, 13). A discussion of the occurrence of selenium in certain Pleistocene deposits of South Dakota has been published recently (9).

Since most Pleistocene deposits of glaciated regions were derived by ice action and later modified by water and wind, Pleistocene materials should include Cretaceous ingredients derived from beds over which glaciers moved. Inclusion of seleniferous Cretaceous chalk and chalky shale from such beds as the Niobrara formation and the upper Virgin Creek and Mobridge members of the Pierre formation would be expected, and drifts and materials derived from drifts in South Dakota, Minnesota, and Iowa should contain selenium, possibly in notable amounts. Selenium has been found in wheat grown on soils of glacial derivation in Saskatchewan (3, 10). Plants containing noteworthy amounts of selenium have been collected from glaciated areas in Montana, North Dakota, and Canada (12, 13). *Astragalus racemosus* Pursh, a selenium "indicator" plant, was noted growing in Pleistocene deposits of northeastern South Dakota in 1941, and analyses indicated the presence of considerable amounts of selenium in many of these plants. Studies of Pleistocene material, soils, and plants were begun in 1942 and were continued and expanded in 1944 and 1945. Bedrock studies were made to assist in determination of possible sources of selenium in Pleistocene deposits.

AREA STUDIED

The area investigated includes all of ten counties and parts of six other counties in northeastern South Dakota (fig. 1). The most detailed studies were made in Brookings, Kingsbury, Hamlin, and Beadle Counties. The area lies along the divide between the valleys of James and Big Sioux Rivers and includes much of the drainage of the upper portions of these streams as well as some drainage into Lake Traverse, Big Stone Lake, and Little Minnesota River. The lake region of South Dakota extends north and south across the middle of the area, which lies on the Coteau des Prairies.

GEOLOGY OF THE AREA

Below the surface, northeastern South Dakota is mantled by five or probably six glacial drifts, glaciofluvial deposits, lacustrine deposits, loess, interglacial sands and gravels, and recent alluvium and soils.   The oldest Pleistocene deposit exposed in the area is the Kansan drift, most of which outcrops along the Big Sioux valley but outliers of which occur elsewhere (fig. 1).   Four drifts of Wisconsin age occur widespread in the area[2]: early Wisconsin, Iowan lies mostly east of Big Sioux River; mid-Wisconsin, Arlington drift forms the lake region

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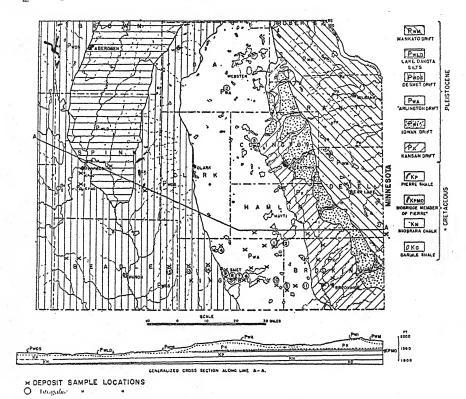
FIG. 1. GEOLOGICAL MAP OF THE AREA STUDIED SHOWING SAMPLE LOCATIONS

which lies between Big Sioux River and the DeSmet drift; late mid-Wisconsin, the DeSmet drift, lies west of the Arlington in and along the valley of James River except where it is covered or displaced by the silts of glacial Lake Dakota (fig. 1); late Wisconsin, or Mankato drift occupies the northeastern part of the area studied.   These deposits have been described elsewhere (9).   Outwashes of silt, sand, and gravel associated with the various drift sheets are important deposits of the area.   Glaciolacustrine deposits other than Lake Dakota deposits also occur and are most common within the area of DeSmet drift where waters were impounded by morainic ridges from time to time.

[2] There is some possibility that the DeSmet drift is Mankato in age.

SELENIUM CONTENT OF DEPOSITS

Analyses for selenium were made on 220 composited samples of 15 glacial and related deposits representing 337 feet of these deposits. Bedrock samples representing 22 feet of materials were similarly investigated. Some ground-water samples and samples of water from ponds were also analyzed for selenium. All selenium determinations were made by the method described by Klein (4).

TABLE 1

Selenium content of Pleistocene deposits and bedrock

DEPOSITS SAMPLED	DEPTH SAMPLED	SELENIUM IN SAMPLES		
		Maximum	Minimum	Average
	feet	p.p.m.	p.p m.	p.p.m.
Kansan and Iowan till (undifferentiated).........	13.5	3.70	0.31	1.33
Arlington glacial till...........................	104.0	4.92	0.20	1.38
Arlington loess.................................	7.5	3.24	0.27	0.76
Soil on Arlington loess........................	4.33	1.87	0.66	1.06
Arlington basin loess and loess-like silts..........	87.75	6.04	<0.05*	1.60
Soil on Arlington basin loess and loess-like silts.....	20.0	8.90	0.59	3.05
DeSmet till....................................	23.0	5.38	0.27	1.13
DeSmet outwash and terrace deposits...........	17.5	1.44	0.12	0.64
Mankato till...................................	5.0	0.86†	0.86†	0.86†
Wisconsin outwash, valley train, and terrace deposits outside of Arlington and Mankato drifts.	29.0	3.72	<0.05*	0.65
Lake Dakota silts..............................	8.0	2.92	1.17	1.83
Mankato lake silts, terrace above Lake Henricks...	5.0	1.75	0.86	1.22
Soil on Wisconsin outwash valley train, terrace deposits outside Arlington and Mankato drifts...	9.0	1.91	<0.05	0.66
Soil on DeSmet outwash........................	2.0	1.51	1.05	1.28
Mankato outwash or lake terrace deposits........	4.0	4.45†	4.45†	4.45†
Bedrock—Uppermost Niobrara from near Sisseton.	5			0.31
Bedrock—Pierre shale, nearly black, from southeast Spink County...........................	5			1.21
Bedrock—Pierre shale, brown mudstone, Jerauld County......................................	4			1.56
Bedrock—Pierre, Mobridge member, from near Redfield, Spink Co............................	3			6.4
Bedrock—Pierre, Mobridge member, near above location....................................	5			15.0

* One 3-foot sample only.

† One sample only.

All glacial deposits of northeastern South Dakota, and probably those of the surrounding regions, contain some selenium (table 1). None of the samples collected, representing 145 feet of till, compositely sampled, were selenium-free. Local maxima reach 3.70, 4.92, 5.38, and 0.86 p.p.m. selenium for undifferentiated Kansan and Iowan, Arlington, DeSmet, and Mankato tills respectively. Since all, or essentially all, of the selenium is contained in the clay fraction of the till (9) these maximum amounts in the fine portion of the till are twice or

more those indicated for till as a whole. On the average, however, the tills contain less than 1.5 p.p.m. selenium.

Arlington loess and loess-like silts, which mantle Arlington till and older deposits except where removed by erosion or covered by later deposits, contain but little selenium in upland or hilltop positions (maximum 3.24 p.p.m., average 0.76 p.p.m.) but in depressions they contain selenium locally in noteworthy amounts (table 1). A maximum of 6.04 p.p.m. selenium was found in a sample of loess-like silt taken from a low topographic position.

The soils formed on this loess and loess-like silt, particularly at low topographic positions, appear to be more seleniferous than the parent materials (maximum 8.90 p.p.m. selenium). The maximum content of selenium in soil on the loess-like silt was 47 per cent greater than the maximum in loess-like silt. The average selenium content of the soils analyzed was nearly 91 per cent greater than averages of the selenium content of the loess-like silts. Outwash and valley train deposits contained selenium in varying amounts up to 3.72 p.p.m. selenium. Glaciolacustrine deposits, mostly silts and sands, and the soils formed on them are of particular interest, as cases of selenium poisoning in farm animals have been observed on them. The most widespread glaciolacustrine deposits of South Dakota are those of extinct glacial Lake Dakota. Two analyses of these deposits indicate a selenium content of 1.17 and 2.92 p.p.m. selenium for 5- and 3-foot composite samples respectively. Another silt deposit associated with Mankato drift, which possibly is glacial outwash rather than lacustrine, contained 4.45 p.p.m. selenium.

A relatively flat area of a few hundred square miles lies in eastern Spink County and western Clark County. Where investigated, this area shows 2 to 6 feet of soil and sand with considerable interstitial clay which lie over glacial till probably of late mid-Wisconsin (DeSmet) age. These sands and clay are believed to have been deposited in a temporary glacial lake lying between the highland of eastern South Dakota known as the Coteau des Prairies and the ice edge to the west which is marked by a glacial moraine passing just west of Iroquois, South Dakota. On one farm in this area several head of cattle showed pronounced symptoms of chronic selenium poisoning in the winter of 1944–45 and cases were reported from a nearby farm during the same period. Analyses of blood from the affected animals showed a selenium content ranging from 2 to 4 p.p.m. Mixed wild hay grown in 1944 contained 12 p.p.m. selenium. Samples of soil, sand, and the underlying glacial till were taken and analyzed for selenium (table 2). Most of the black soils contain so little selenium where they were sampled (0.63 p.p.m. to 0.79 p.p.m. selenium) that they can not be regarded as a probable source for the selenium found in hay on the farm. The sand likewise contains but little selenium, except in one sample (table 2, hole 4, 2–4 foot depth) where it contained 1.11 p.p.m. selenium. The glacial till underlying the sand is also low in selenium (table 2).

Of four composite samples of sand on the glacial drift, three contained selenium but in relatively small amounts (0.36 to 0.59 p.p.m. selenium). The fourth, however, contained 1.11 p.p.m. selenium (table 2). Were this amount of

selenium distributed throughout the sand, the content would probably be too small to produce toxic vegetation. Previous studies indicate, however, that most if not all of the selenium is contained in the clay and silt fractions. Clay and silt was separated from these sand samples by the subsidence method (11)

TABLE 2

Analyses of samples of lacustrine sand, soil, and glacial till collected in western Clark County, South Dakota

HOLE NO.	DEPTH	DESCRIPTION	SELENIUM	SILT AND CLAY	SELENIUM IN SILT AND CLAY
	feet		*p.p.m.*	*per cent*	*p.p.m.*
1	3–5	Sand, buff to light brown, with considerable buff clay interbedded in thin beds. Crystalline salts abundant in places, some in vuggs. A little yellow to brown limonite	0.59	31.3	1.19
	5–7	Till, gray to brown, mostly gray with limonite spots, root tubes with dark brown center surrounded with iron oxide stain to more than ¼ inch in diameter. Tough, with many small shale pebbles. Considerable salt accumulation, some in vuggs. Much clay			
2	1.5	Soil, black, plastic when moist, no pebbles, some sand grains	0.79		
	1.5–2.5	Clay, mottled light and dark gray, plastic	0.47	23.3	2.02
	2.5–3	Till, light to medium gray, tough, small pebbles including many of dark shale. Vermillion, bright red to brown mottling. Considerable quantity of white salts			
3	1.5	Black loam, powdery	0.75		
	1.5–5	Sand, with much clay, buff or light brown, one kindschen ¼ inch in diameter (live grass root at five feet)	0.36	31	1.16
4	0–2	Black sandy loam, some white salts in lower few inches	0.63		
	2–4	Sand, buff, silty salts so abundant that powdered sample has light gray cast	1.11	18.3	6.07
	4–5	Till, medium gray to buff, pebbles small, dark shale pebbles numerous. Crystalline salts abundant in spots	0.40		

and the percentage of the fine fraction appears in table 2. The silt and clay fractions taken together in this sample contain 6.07 p.p.m. selenium. Concentrations of this magnitude are believed by the authors to be capable of furnishing from 3 to 12 p.p.m. of selenium to western wheat grass (*Agropyron smithii* Rydb.) or even more under most favorable conditions. Grasses that

average more than 5 p.p.m. selenium are potentially dangerous to livestock. It should be noted that *Agropyron smithii* Rydb. under favorable conditions may take up amounts of selenium three to nearly six times that contained in the third foot of soil.

SOURCES OF SELENIUM IN PLEISTOCENE DEPOSITS

The source of selenium in glacial drift and its derivatives, such as outwash, alluvium, glaciolacustrine, and probably some of the material constituting the loess, is the bedrock or older drifts over which the glaciers have moved. Seleniferous Cretaceous chalk, the Mobridge member of the Pierre formation, in northeastern South Dakota has previously been noted (9) in Spink County. The distribution of this seleniferous member below the drift is unknown, but it is certain that it lies below the drift along the west slope of the Coteau des Prairie and possibly elsewhere under the Coteau where it was available for incorporation into drift by the moving ice. The selenium in the loess and loess-like silts may have been derived in part from glacial drift by wind erosion. Since these deposits, or deposits indistinguishable from them, occur westward to and beyond the Missouri River valley, the source of much of the loess is believed to be the unglaciated bedrock west of Missouri River. The Mobridge member of the Pierre formation is exposed over wide areas west of Missouri River in South Dakota (8) and it is believed to be the source of a large part of the selenium in the loess and loess-like silts of northeastern South Dakota.

SELENIUM CONTENT OF *Astragalus racemosus* PURSH GROWING IN THE AREA

The selenium content of samples of *Astragalus racemosus* Pursh which have been collected from the various locations (fig. 1) is shown in table 3. Considerable variation in selenium content is shown in samples from the same location grown in different years. All samples which contained over 1,000 p.p.m. of selenium were collected from poorly drained, low topographic positions (map locations 4, 10, and 13). The selenium content of the *Astragalus racemosus* Pursh plants growing in these three locations is as high as is ordinarily encountered in these plants when they have been collected in toxic areas on Cretaceous formations (7, 8). The range in selenium content of the *Astragalus racemosus* Pursh samples is as wide as the range in selenium content of *Astragalus bisulcatus* (Hook.) Gray and *Astragalus pectinatus* Dougl. collected in Montana by Williams, Lakin, and Byers (12). The same authors (13) have reported a selenium content of 3,240 p.p.m. for *Asiragalus bisulcatus* growing on glacial drift in Saskatchewan.

Although the selenium content of the *Astragalus* plants is comparatively high in some of the locations, no evidence of selenium poisoning in livestock has been observed in the vicinity of any of the locations shown on the map. A sample of white clover, *Trifolium repens* L., collected in June, 1945, at map location 10 contained only 1.07 p.p.m. selenium, whereas the *Astragalus racemosus* Pursh growing within 3 feet of the clover contained 1,788 p.p.m. of selenium. No *Astragalus* plants were observed in the vicinity of farms near the

Clark-Spink County line where livestock showed symptoms of selenium poisoning.

Samples of surface water were taken from ponds at two of the *Astragalus*

TABLE 3
Selenium content of Astragalus racemosus *Pursh growing in Pleistocene deposits*

DEPOSIT	MAP LOCATION	DATE SAMPLED	TOPOGRAPHIC POSITION	SELENIUM CONTENT
				p.p.m.
	1	July, 1942	high	312.8
	1	July, 1942	high	45.6
	1	July, 1942	high	277.7
	1	July, 1942	high	37.8
	1	July, 1942	high	154.5
	2	July, 1942	high	154.2
Arlington till	2	June, 1944	high	340.2
	2	June, 1945	high	418.0
	3	July, 1942	high	351.8
	4	July, 1942	low	2,000.0
	4	June, 1944	low	812.2
	4	June, 1945	low	322.0
	5	July, 1941	high	16.0
	5	July, 1942	high	64.9
	5	June, 1943	high	
	5	June, 1945	high	5.9
	6	July, 1942	low	575.0
	6	July, 1943	low	381.0
	7	July, 1942	low	400.0
	8	July, 1942	low	500.0
Arlington loess	8	July, 1943	low	102.4
	8	June, 1944	low	152.1
	9	July, 1941	low	310.0
	10	July, 1942	low	2,920.0
	10	July, 1943	low	2.374.0
	10	June, 1944	low	3,134.0
	10	June, 1945	low	1,788.0
	11	June, 1944	low	401.7
	12	July, 1944	low	5.5
	13	July, 1941	low	1,570.0
DeSmet drift	14	July, 1941	low	320.0
	15	July, 1943	medium	131.6

locations in 1942. The sample from map location 10 contained 21.4 p.p.b.[3] selenium and the sample from map location 4 contained 85.5 p.p.b. Ground-water samples taken from two borings near the pond at map location 10 contained 80.9 and 760.0 p.p.b. selenium. As the water was within about 5 feet

[3] p.p.b. = parts per billion.

of the surface in both borings, the selenium in this ground water would be available for the *Astragalus* plants grown at this location.

SUMMARY

Investigations were made of Pleistocene deposits, soils, plants, and bedrock materials in relation to selenium content and the source of the selenium. The area studied included all of ten counties and parts of six other counties in northeastern South Dakota.

Selenium determinations were made on 220 composited samples of 15 glacial and related deposits and on samples representing 22 feet of bedrock.

None of the till samples were selenium-free. Local maxima reach 3.70, 4.92, 5.38, and 0.86 p.p.m. selenium for undifferentiated Kansan and Iowan, Arlington, DeSmet, and Mankato tills, respectively. On the average the tills contain less than 1.5 p.p.m. selenium.

Arlington loess and loess-like silts contain little selenium in upland and hilltop positions, but in depressions they contain selenium in noteworthy amounts.

Soils formed on loess and loess-like silts, particularly at low topographic positions, appear to be more seleniferous than parent materials. The average selenium content of the soils analyzed was nearly 91 per cent greater than the average selenium content of the loess-like silts.

Outwash and valley train deposits contained selenium in varying amounts up to 3.72 p.p.m.

Several head of cattle on one farm in the area showed pronounced symptoms of chronic selenium poisoning in the winter of 1944–45.
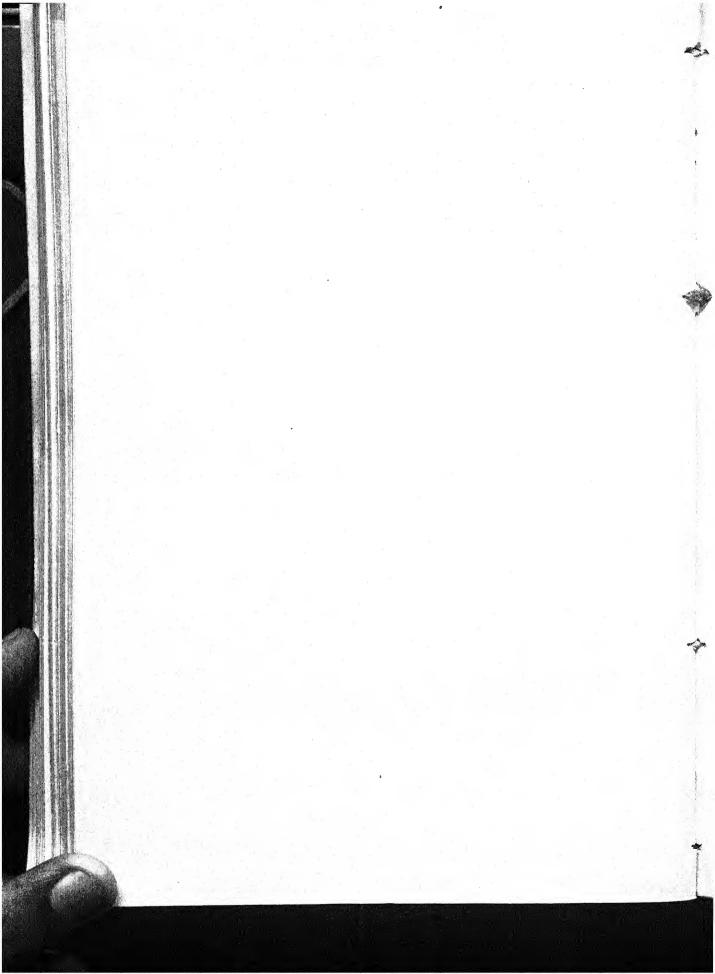
Considerable yearly variation was found in selenium content of *Astragalus racemosus* Pursh samples grown in the area studied. All samples containing over 1,000 p.p.m. selenium were found growing in poorly drained, low topographic positions; pond water and ground water at these locations contained appreciable amounts of selenium in solution.

A discussion is given of the probable sources of the selenium in the Pleistocene deposits and soils developed thereon.

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RELATION OF PARENT MATERIAL AND ENVIRONMENT
TO THE CLAY MINERALS IN IOWA SOILS[1]

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In places along the lower Des Moines River in Iowa, the Pleistocene overload is so thin that the soils are formed either entirely or partly from shales and clays of the Pennsylvanian system. These soils are characterized by a smooth, soapy feel and by the imperviousness of their lower horizons. They are subject to such erosional processes as earth creep and slumping and frequently show such erosional forms as stepped crescents, terracettes, scarps, and slumps (8). Because these properties seemed to depend on the clay portion of these soils, a study was initiated to determine the differences between these clays and those of the Pleistocene deposits, which are the predominant parent materials in Iowa.

EXPERIMENTAL PROCEDURE

It was decided to prepare differential thermal curves for the clays from profile samples of two sites within the Gosport soil series, the series most typical of those Iowa soils influenced by Pennsylvanian sediments. The curves prepared are shown in figure 4 in comparison with similar curves previously prepared for other Iowa soils (7) all of which were derived from Pleistocene materials.

The soils used in the study may be described briefly as follows: The Marshall, Tama, Shelby, and Clarion are all prairie soils. The Marshall and Tama are found on Peorian loess, the former in the western part of the state where the rainfall is lower and where the main source of the loess has been the silt from the Missouri River Valley, and the latter in eastern Iowa where the rainfall is higher (fig. 1) and the loess has come largely from the Iowan drift (3). The Clarion occupies the rolling, well-drained upland of the Wisconsin drift, and the Shelby the sloping hillsides of southern Iowa where the Kansan and Nebraskan tills are not covered with loess. These tills with their interglacial deposits are the oldest Pleistocene materials in the state (fig. 2). The Webster is a Wiesenboden and is the poorly drained member of the Clarion-Webster catena. The Clinton is a gray-brown podzol found in the loess of northeastern Iowa. The Gosport is derived from the sedimentary rocks of the Des Moines series of the Pennsylvanian system (fig. 3) where they have been exposed on hillsides by erosion or from a shallow layer of Pleistocene material underlain by Pennsylvanian rock. It is generally a gray-brown podzol or a soil transi-

tional between prairie and gray-brown podzolic. The Pennsylvanian deposits are predominantly clays and shales with a few layers of sandstone and of coal and an occasional layer of limestone.
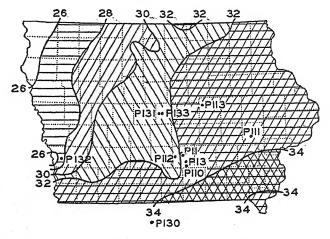

FIG. 1. NORMAL ANNUAL PRECIPITATION (INCHES) FOR IOWA
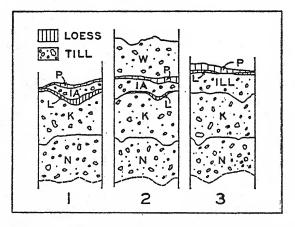Location of profile samples shown by circles. Taken from Thom and Fletcher (10).

FIG. 2. CROSS SECTIONS SHOWING RELATIONSHIPS OF PLEISTOCENE DEPOSITS IN IOWA
1. Representative section for western Iowa; 2. Representative section for north-central Iowa; 3. Representative section for southeastern Iowa.
IA, Iowan drift; Ill, Illinoian drift; K, Kansan drift; L, Loveland loess; N, Nebraskan drift; P, Peorian loess; W, Wisconsin drift.
Adapted from Kay and Apfel (2).

In order to characterize more completely the clay mineral composition of the clay fractions, x-ray diffraction photographs were prepared and base-exchange studies made of selected samples of the Gosport profile and of other profiles used in the comparison as listed in tables 1 to 4, inclusive.
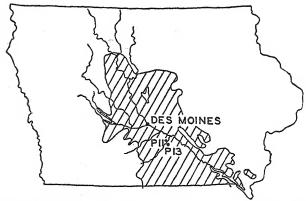
FIG. 3. DES MOINES SERIES OF THE PENNSYLVANIAN SYSTEM

Principal area in Iowa where the Pleistocene deposits are underlain by the Des Moines series of the Pennsylvanian system. Gosport soils occur south of Des Moines on hillsides where little or no till overlies the Pennsylvanian sediments. Location of Gosport samples are shown by circles. Adapted from Kay and Apfel (2).

TABLE 1

Interplanar spacings for B horizons of a soil weathered from Pennsylvanian shale and one weathered from recent Pleistocene material

MINERAL*	GOSPORT SILTY CLAY LOAM P-13 21 TO 27 INCHES (FROM PENNSYLVANIAN SHALE)		WEBSTER LOAM P-133 33 TO 35 INCHES (FROM WISCONSIN DRIFT)	
	25°C.	500°C.	25°C	500°C.
	A.	*A.*	*A.*	*A.*
M			15.70 s.	
MI				10.20 w.
I?	10.00 v.v.w.†			
K	7.40 v.v.w.			
IMK	4.52 s.	4.50 s.	4.50 s.	4.50 s.
Q	4.28 v.v.w.			
Q	3.36 m.	3.38 m.	3.37 m.	3.35 m.
CIM	3.00 w.		3.05 m.	diffuse $\begin{Bmatrix} 2.59 \\ 2.46 \end{Bmatrix}$ m.
KIM	2.59 s.	2.59 w.	2.58 s.	
KR	2.47 v.v.w.	2.48 v.v.w.		
K	2.36 v.v.w.			
Q	2.26 v.v.w.	2.26 v.v.w.	2.28 v.w.	2.26 v.w.
K	2.01 v.v.w.			
Q			1.81 v.v.w.	1.82 v.v.w.
KMQ	1.68 v.w.	1.69 v.w.	1.69 w.	1.72 w.
IKM	1.50 s.	1.52 v.w.	1.50 s.	1.51 m.
Q	1.38 v.v.w.	1.38 v.v.w.	1.38 v.w.	1.38 v.w.
MKI	1.29 v.v.w.	1.30 v.v.w.	1.30 m.	1.30 v.w.
MK	1.24 v.v.w.	1.25 v.v.w.	1.24 v.w.	1.26 v.w.

* C, Calcite; R, rutile; I, illite; K, kaolinite; M, montmorillonite; and Q, quartz. The letter merely signifies that the line may be caused by that mineral.

† Relative intensities of the x-ray reflections: v.s., very strong; s., strong; m.s., medium strong; m., medium; w.m., weak to medium; w., weak; v.w., very weak; and v.v.w., very, very weak; and ?, doubtful.

For the x-ray analyses, clay fractions with a maximum particle size of 1 μ diameter were prepared by gravity sedimentation. The clay suspensions were filtered through Pasteur-Chamberland tubes. The clays were dried and ground

TABLE 2

Effect of partial dehydration on the interplanar spacings of colloids from Iowa soil profiles

SAMPLE	HORIZON	DEPTH	TEMPERA-TURE	MONTMORIL-LONITE SPACINGS	KAOLINITE SPACINGS	ILLITE SPACINGS
		inches	°C.	A.	A.	A.
P13 Gosport silty clay loam	A	3–6	25	None	7.5	None
			500	None	None	None
	B	21–27	25	None	7.4	10.0 ?
			500	None	None	None
P11 Pennsylvanian clay	C	50	25	16 ?	7.5	None
			500	10.0	None	10.0 ?
P111 Clinton silt loam	A	3–6	25	14.0	None	None
			500	9.8	None	None
	B	42	25	16.0	None	None
			500	10.3	None	10.3 ?
P113 Tama silt loam	A	6–7	25	15.5	None	None
			500	10.3	None	10.3 ?
	B	26–36	25	15.0	None	None
			500	10.2	None	10.2 ?
P131 Clarion loam	A	6–17	25	16.0	None	None
			500	10.3	None	10.3 ?
	B	31–33	25	14.9	None	None
			500	9.8	None	None
P133 Webster loam	A	10–12	25	13.0	None	None
			500	10.0	None	10.0 ?
	B	33–35	25	15.7	None	None
			500	10.2	None	10.2 ?
P132 Marshall silty clay loam	A	0–5	25	17.0	None	None
			500	10.34	None	10.34 ?
	B	26	25	16.4	None	None
			500	10.0	None	10.0 ?
Deep loess	C	120	25	13.5	None	None
			500	10.3	None	10.3 ?

to pass a 60-mesh sieve, and part of each sample was used without further chemical treatment. X-ray diffraction patterns were obtained by packing the colloids in thin-walled soft-glass tubes of about 0.4 mm. diameter and exposing them to K α molybdenum radiation filtered through a zirconium screen.

For the thermal analyses, the clays were prepared in the same way and then mixed with H_2O_2 and with NaBrO (11) to remove organic matter, saturated with Ca from $1\ N\ Ca(C_2H_3O_2)_2$, adjusted to pH 7, and freed of excess Ca by repeated leachings with a solution of 4 parts methyl alcohol and 1 part water. Part of this sample was used for the thermal analysis and part was analyzed for Ca as a measure of exchange capacity.

TABLE 3

Estimates of the relative amounts of clay minerals present in 1 μ fractions from Iowa soil profiles

SOIL	HORIZON	DEPTH	QUARTZ	CALCITE	KAOLINITE	MONTMORIL-LONITE	ILLITE
		inches					
P 13 Gosport silty clay loam	A	3–6	+++++*	0	+++++	+?	+?
	B	21–27	+++	+	+++++	+?	+
P 11 Pennsylvanian clay	C	50	+++++	0	+++++	+	+?
P 111 Clinton silt loam	A	3–6	+++++	0	+?	+++++	0
	B	42	++	0	+?	+++++	0
P 113 Tama silt loam	A	6–7	+++++	0	+?	+++++	0
	B	26–36	+++	0	+?	+++++	0
P 131 Clarion loam	A	6–17	+++++	0	+?	+++++	0
	B	31–33	++++	0	+?	+++++	0
P 133 Webster loam	A	10–12	+++	+++++	+?	+++++	0
	B	33–35	+++	+++	+?	+++++	0
P 132 Marshall silty clay loam	A	0–5	++++	0	+?	+++++	+?
	B	26	+++	0	+?	+++++	+?
Deep loess	C	120	+++	+	+?	+++++	+?

* Estimated relative abundance of the different minerals shown as follows: +++++ > ++++ > +++ > ++ > + > 0 where +++++ indicates evidence of greatest abundance, and 0 the lack of any evidence of the mineral's presence. Estimates are based on interpretation of interplanar spacings and intensities of x-ray diffraction lines.

RESULTS AND DISCUSSION

In the differential thermal analysis of clay minerals, the extent of the endothermic deflections characteristic of either montmorillonite or kaolinite has been found to be proportional to the amount of causative mineral present (7, 9). On this basis, a comparison of the thermal curves for the profiles shown in figure 4 reveals that where the parent materials of the Gosport soils are clay or shale of the Des Moines series of the Pennsylvanian system, the clay fraction is predominantly kaolinite. The unusually high kaolinite content of the clay

of these parent materials distinguishes these soils from other Iowa soils which for the most part have developed from Pleistocene deposits and, according to this and other studies (7, 9), usually have a high proportion of montmorillonite in the clay.   Since the unweathered Pennsylvanian clays and shales of the Des Moines series are apparently almost pure kaolinite (60-inch depth, P-13, and 47–50-inch depth, P-11, fig. 4), it may be judged from the thermal curves that profile P-13 has weathered from such sediments and is little if any contaminated with Pleistocene material.   P-11, on the other hand, appears to have formed in shallow till over Pennsylvanian shale.

Like other forest soils in the state such as the Clinton (P-110 and P-111, fig. 4), P-13 shows an increase in montmorillonite with depth in the profile, although the amounts are small in comparison with the proportion of kaolinite

TABLE 4
Base-exchange capacities of 1μ clay fractions from Iowa soil profiles

SAMPLE	HORIZON	DEPTH	REPLACEABLE Ca PER 100 GM. CLAY
		inches	*m.e.*
P 13 Gosport silty clay loam	A	3–6	33.5
	B	21–27	29.2
P 11 Pennsylvanian clay	C	50	37.1
P111 Clinton silt loam	A	3–6	61.9
	B	42	64.8
P113 Tama silt loam	A	6–7	84.0
	B	26–36	74.5
P133 Webster loam	A	10–12	78.5
	B	33–35	55.7
P132 Marshall silty clay loam	B	26	73.7
Deep loess	C	120	54.9

in the clay.   In P-11 the marked deflections for both kaolinite and montmorillonite in the upper profile resemble those of the Shelby (P-130, fig. 4), which is a prairie soil formed from the same glacial deposit as that overlying the sediments in the Gosport at this location.   Apparently the stratum of clay underlying this till is of almost pure kaolinite.

When the thermal curves of figure 4 are considered in relation to the characteristics of the soils they represent, it can be seen that the distribution of montmorillonite and kaolinite within the profiles varies with parent material, age, and environment of the soils.

The clays of two profiles in the relatively recent Wisconsin drift, the Webster and Clarion loams, show no appreciable shifts in composition in respect to kaolinite and montmorillonite with depth in the profile.   On the other hand, soils formed on the loess, which—except for a possible few inches at the surface—
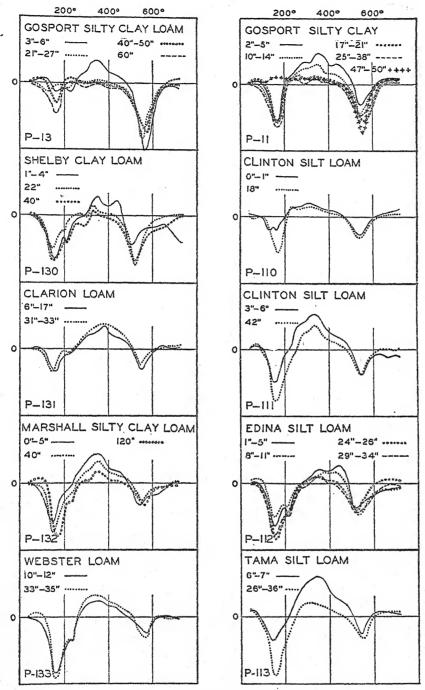
FIG. 4. DIFFERENTIAL THERMAL CURVES OF THE CLAY FRACTIONS OF SOME IOWA
SOIL PROFILES
Curves for all except the Gosport soils adapted from Peterson (7)

was laid down prior to the Wisconsin (2 and 3 of fig. 2), show a shift in favor of montmorillonite with depth. In a profile of Marshall silty clay loam from southwestern Iowa this shift is slight, but it is quite marked in one of Tama silt loam from northeastern Iowa where the rainfall is from 4 to 6 inches higher (10). Since these two loessial prairie soils are considered to be rather similar in respect to source material and time of deposition (2, 3), the shift in clay mineral content in the Tama is thought to reflect more advanced illuviation resulting from the greater rainfall. This tendency for an increase in the amount of montmorillonite in the clay of the B horizon as compared to the A has been found to be a consistant characteristic of Iowa soils with grayish colored, platy structure A_2 horizons, such as the forest soils of the eastern part of the state and the planosols of the south-central area (7, 9).

In the much older (2) Kansan and/or Nebraskan till (fig. 2) a prairie soil, the Shelby, shows more kaolinite throughout the profile than is found in the profiles of the soils of the recent deposits; for example, in the Peorian loess and the Wisconsin drift. This has been found true also of the Lindley, a forest soil occurring in the same drift as does the Shelby (7). Because the original composition of the parent materials is not known, deductions concerning pedogenic shifts in the proportions of kaolinite and montmorillonite in the clay fractions of soil profiles cannot be made with certainty. On the basis of the results of this study and of others (7, 9), however, it seems that the proportion of kaolinite to montmorillonite in Iowa soils tends to increase with weathering, being higher in eluviated horizons and in the older soils.

The x-ray diffraction pictures verify the high occurrence of kaolinite in the Gosport soils as compared with the soils of Pleistocene origin. They also show that either montmorillonite or kaolinite is the predominating mineral in the various clay samples from these Iowa profiles.

In table 1 is presented a complete summary of the interplanar spacings for the clay fractions of a sample from the B horizon of Gosport silty clay loam, P-13, and of one from the B horizon of Webster loam, P-113. The absence of lines in the vicinity of the 15 A. spacing in the diffraction pattern of the B horizon of the Gosport shows that montmorillonite is lacking or present in small amounts (1, 4, 12). Kelley (5) has shown that in mixtures of minerals, less than 10 per cent of montmorillonite will not produce diffraction lines definite enough to be measured. The presence of a 7.4 A. line for the air-dry sample and its absence in the 500° sample are proof of the presence of kaolinite. The very, very weak 10 A. line for the air-dry sample may indicate the presence of illite, although the disappearance of this line on heating is not typical of that mineral.

The clay fraction of the B horizon of Webster loam is shown to be predominantly montmorillonitic by the presence of a strong line at the 15.7 A. spacing which is replaced on heating to 500° by a line at 10.2 A. The absence of appreciable quantities of illite is apparent from the absence of a 10 A. line in the air-dry sample. This does not entirely preclude the presence of illite, because it has been demonstrated (12) that at least 10 per cent of the clay must be illite

before that mineral can be detected by x-ray diffraction lines. The lack of a 7 A. line is indicative of the absence of kaolinite. The diffraction lines in both the Webster and the Gosport which occur at 3.35 to 3.38 A., at 2.45 to 2.48 A., and at 1.38 A. spacings show the presence of considerable quantities of quartz in both samples. Colloids separated by sedimentation may be expected to contain quartz and other minerals entangled by aggregation of the clay particles (4).

Because they are more reliable as guides in identification (4), only the wide spacings are shown in the summary of diffraction lines for the clays (table 2).
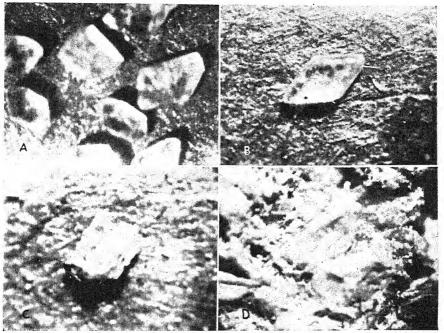
FIG. 5. CRYSTALS OF GYPSUM FROM A CLAY STRATUM OF THE DES MOINES SERIES OF THE PENNSYLVANIAN SYSTEM

A. Cluster of crystals removed from the clay; B. Twinned crystal; C. Dovetailed crystal; D. Crystals lining the wall of a soil cavity. Magnification 10×.

An estimate of the relative abundance of certain minerals in the clay fractions is given in table 3. In the preparation of this table, the intensities of the diffraction lines and the presence or absence of certain key lines were taken into consideration. This technique is only approximately quantitative (4, 12) because of the technical difficulties in the method and because of the variability in intensity encountered with samples from the same clay mineral and with differences in particle size and aggregation. Nevertheless, the evidence of preponderance of kaolinite in the clay from the Gosport and its parent material and of montmorillonite in the other soils from Iowa, all of which were derived from Pleistocene material, is definite.

This analysis is substantiated by the values for the base-exchange capacities of the various clays from the profile samples shown in table 4. Characteristically low capacities are found for the kaolinitic clays.

The layers of kaolinitic clay in the C horizons of the Gosport soils were observed to be dense and compact. Virtually all root growth stops at the first unweathered clay layer, and the products of illuviation pile up above the line of demarcation between the compact layer of clay and the overlying soil profile (8). Thin sections of these clay layers show them to be almost devoid of cracks or pore spaces. The occurrence of this layer of impervious material beneath a more pervious covering which has been ameliorated by processes of soil formation may account for the susceptibility of such soils to earth flow and slumping (8).

A characteristic of the clays and shales of this region is the presence of gypsum crystals and nodules of pyrites. The gypsum usually occurs as fine crystals filling small cavities in the clay (fig. 5). In some places crystals 10 to 20 cm. long are found, which often show very marked twinning and characteristic dovetailing. In view of the opinion that kaolinite may be formed by the action of sulfuric acid derived from pyrites and acting on aluminous materials (6), the presence of gypsum crystals and pyrites in these kaolinitic sediments suggests that these clays may be the product of a similar process.

SUMMARY

The clay minerals of several Iowa soils were studied by differential thermal analysis, x-ray diffraction pictures, and analysis of base-exchange capacity.
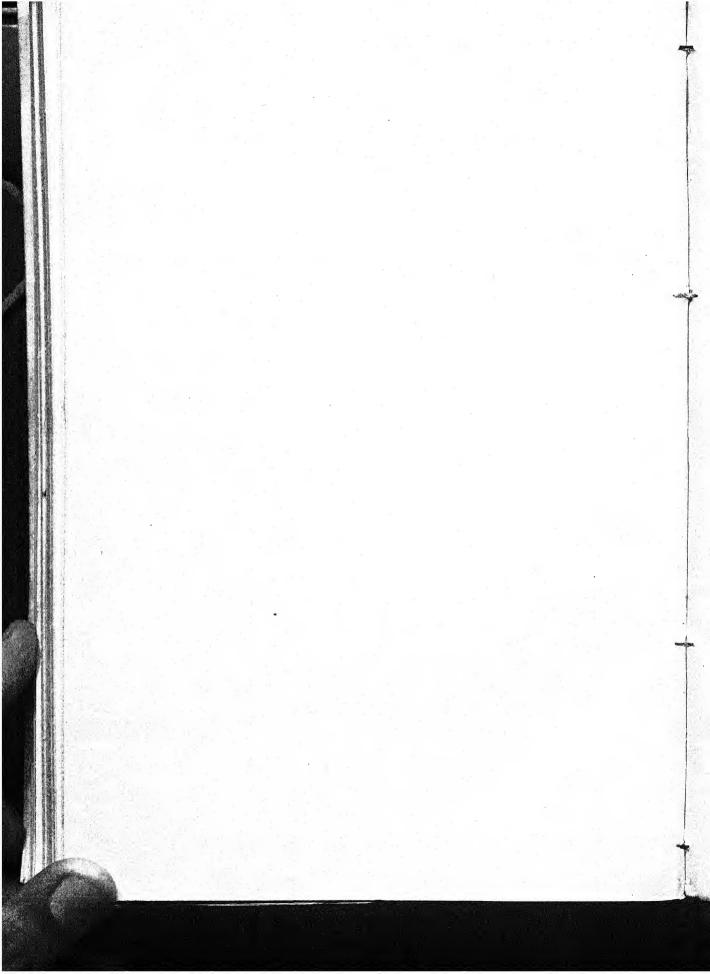
Iowa soils with parent material of Pleistocene origin, which includes most of the soils of the state, are characteristically high in montmorillonite. The proportion of montmorillonite to kaolinite in these profiles was found, however, to vary according to climate, vegetation, and source and age of the parent material.

If the profiles studied are typical, they indicate that there is little difference between the A and the B horizons of either prairie or wiesenboden soils of the Wisconsin drift in respect to the kinds and amounts of clay minerals in the clays. Generally in soils on older Pleistocene materials the proportion of montmorillonite to kaolinite is lower in the A and higher in the B, this shift being greater in the gray-brown podzols and planosols than in the prairie soils. There is also evidence that the increase in montmorillonite in the clay of the B horizon is greater in areas of greater rainfall.

Soils of the lower Des Moines River Valley, represented by the Gosport series, contain layers of Pennsylvanian clay or shale in the parent material of their horizons. These soils are characterized by erosional forms such as slump scarps and terracettes which result from mass movement of the more porous upper layers along the surface of the impervious clay layers. These Pennsylvanian clays and shales are predominantly kaolinite, which is thought to account for their compactness and imperviousness.

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EFFECT OF DIFFERENT SOURCES OF NITROGEN ON SOIL REACTION, EXCHANGEABLE IONS, AND YIELDS OF CROPS[1]

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During the period 1928 to 1930, a number of field experiments were started in Alabama on the various substations and experiment fields for the purpose of studying the efficiency of different sources of nitrogen for the production of cotton and corn. In 1941, after these experiments had been conducted for 11 to 13 years, it was decided to make a chemical study of the soils on all the plots. The data reported herein are the results obtained from chemical analyses of these soils together with a summary of the yields of crops obtained for the period.

Undoubtedly, investigators have given more attention to the effect of various sources of nitrogen on soil reaction than to its effect on other soil factors (4, 6, 7, 10, 13, 14, 16). Published data (1, 2, 3, 15, 18) show that, when acidity was corrected with neutralizing materials, the usual differences in crop yields resulting from the application of different sources of nitrogen were eliminated in most cases. Allison and Cook (1) have indicated that 1.43 pounds of calcium carbonate was required to neutralize the acidity developed in the soil by the application of 1 pound of ammonium sulfate, and Pierre's data (11) showed that 1.2 pounds of calcium carbonate or 2.2 pounds of basic slag was sufficient. It has also been shown by Tidmore (15) and Pierre (11) that a mixture in which about 70 to 75 per cent of the nitrogen was in the form of sodium or calcium nitrate and 25 to 30 per cent in the form of ammonium sulfate maintained the soil at a constant pH.

Acid-forming fertilizers used on acid soils reduced the availability of native soil phosphorus, but physiologically basic fertilizers increased the availability of phosphorus, according to Fudge (5) and Tidmore (15). Mixtures of ammonium sulfate and superphosphate produced less cotton (15) than did mixtures of sodium nitrate and superphosphate, but mixtures of ammonium sulfate and basic slag produced more cotton than did mixtures of sodium nitrate and basic slag. Fudge (5) also concluded that acid-forming fertilizers increased the availability of soil potassium at the cost of the potentially available supply.

The hydrogen-ion concentration in the exchange material was found to increase with the continued use of acid-forming fertilizers (15), and it was shown by

Naftel (8) that nitrification of ammonium sulfate was proportional to calcium saturation of the soil.

Results obtained by Pierre (9) from the application of acid-forming fertilizers indicated that the growing of crops had an insignificant effect on the total amount of acid formed in the soil. That is, the important factor was the oxidation of the ammonia-ion to the nitrate-ion, not the removal of the bases by the plants. A method for determining the acidity and basicity of fertilizers has been developed by Pierre (12).

DESCRIPTION OF FIELD EXPERIMENTS

Between 1928 and 1930 standard tiers of field plots were started at the main station on Norfolk sandy loam; at the Tennessee Valley substation on Decatur clay; at the Wiregrass substation on Norfolk fine sandy loam; at the Sand Mountain substation on Hartsells very fine sandy loam; at the Lafayette experiment field on Cecil clay; and at the Monroeville experiment field on Orangeburg fine sandy loam. The Alabama standard tier consists of 34 one-twentieth acre plots. When plots 1A to 17A, inclusive, were laid out from left to right, plots 1B to 17B were laid out from right to left, and *vice versa*. The plots on the "B" side of the tier received exactly the same treatments as the corresponding plots on the "A" side; thus, all treatments were in duplicate. The first plot and every fourth plot thereafter was a check plot, making a total of 10 check plots out of a total of 34. It is believed that the experimental design is adequate for detecting relatively small soil differences and for measuring differences in yields of economic significance. The site for each tier was carefully selected in order to obtain as uniform a piece of land as could be found at each location.

Fertilizer treatments and the methods of applying the fertilizer are given in the tables. All the fertilizer not applied as a side-dressing was applied in a band in a fairly deep furrow and was bedded on before planting. The rows of cotton or corn were located in exactly the same places each year; in plowing, special care was taken to move as little soil as possible from one plot to another.

Only seed cotton and ear corn were removed from the plots; the stalks and other crop residues were plowed under.

METHOD OF SAMPLING THE PLOTS

The center two-thirds of each plot was sampled to a depth of about 7 inches (plow depth) in the spring before the land was plowed, so that the crop rows could be located easily. For all but two tiers on Hartsells very fine sandy loam, a composite sample of soil was taken from each plot by going diagonally across the plot twice from corner to corner, the samples being taken alternately from the middles and from the rows. Care was taken not to bore too close to the band of fertilizer placed in the row the previous season. Twenty-two borings were obtained from each plot, were thoroughly mixed, and a quart aliquot was shipped to Auburn for analysis.

In the two tiers on Hartsells fine sandy loam, the soil taken from the rows was

kept separate from that taken from the middles; thus two composite samples were obtained and analyzed separately.

Samples from duplicate plots ("A" and "B" tiers) were analyzed separately.

CHEMICAL METHODS

The pH values of the soils were obtained, by means of the glass electrode, on a 1 to 2.5 soil:water suspension after standing 2 hours.

Exchangeable hydrogen was determined by extracting 15 gm. of the soil with 300 cc. of normal calcium acetate (pH 7.0) and titrating the leachate with 0.05 N sodium hydroxide. The exchange capacity was determined by measuring the amount of calcium that the soil adsorbed when 15 gm. of soil was leached with 300 cc. of calcium acetate. The adsorbed calcium was removed by leaching the soil with 300 cc. of normal ammonium acetate (pH 6.8). The displaced calcium was precipitated as the oxalate, and the precipitate was oxidized with 0.05 N potassium permanganate, a microchemical technique being used.

Exchangeable calcium and magnesium were removed from the soil by leaching 20 gm. of soil with 300 cc. of normal ammonium acetate (pH 6.8). The magnesium in the leachate was determined by using an 8-hydroxyquinoline microchemical technique, and the calcium was determined as previously described. Potassium was determined according to the method of Volk (17).

EFFECT OF DIFFERENT SOURCES OF NITROGEN ON YIELDS OF SEED COTTON AND CORN

At all six locations and in all nine tests, it is possible to compare only the three plots shown in table 1. It is apparent that 36 pounds of nitrogen applied as sodium nitrate doubled the yield of seed cotton and more than doubled the yield of corn. Each pound of nitrogen produced 18.8 pounds of seed cotton or 0.55 bushel of corn. It is also apparent that ammonium sulfate applied without lime was less efficient than sodium nitrate.

At two locations (table 2) a comparison can be made showing that a mixture in which three fifths of the nitrogen was derived from sodium nitrate and two fifths from ammonium sulfate was slightly more efficient than either ammonium sulfate or sodium nitrate alone. This result was probably due to a combination of the neutralizing effect of sodium nitrate and the benefit derived from sulfur and sodium, both of which are deficient in many Alabama soils.

Eight sources of nitrogen can be compared at three locations (table 3). It will be noted that ammo-phos-A produced distinctly lower yields of seed cotton than did ammonium sulfate, even though the latter made the soil more acid. Results obtained in another experiment indicate that a deficiency of sulfur becomes evident when ammo-phos-A is used continuously as a source of phosphorus and nitrogen. Calcium cyanamid was not quite so efficient as sodium nitrate, calcium nitrate, urea, or cottonseed meal for the production of seed cotton. The exact reason for this is not known, but it may have been due to the slow availability of cyanamid nitrogen.

At five locations the six sources of nitrogen shown in table 4 can be compared. Again, ammonium sulfate, ammo-phos-A, and calcium cyanamid gave low results, but sodium nitrate, calcium nitrate, and urea were virtually identical in efficiency.

TABLE 1

Effects of different sources of nitrogen on yields of seed cotton and corn and on chemical composition of soil

Averages of results from nine experiments at six locations*

FERTILIZER TREATMENT†	AVERAGE YIELDS OF CROPS PER ACRE, 1928 TO 1941		pH OF SOIL AT END OF EXPERIMENT‡	EXCHANGEABLE CATIONS PER 100 GM. SOIL AT END OF EXPERIMENT§			
	Seed cotton	Corn		H	Ca	Mg	K
	lbs.	bu.		m.e.	m.e.	m.e.	m.e.
No nitrogen..............	699	14.2	5.9	1.89	2.01	.23	.29
$(NH_4)_2SO_4$...............	1,267	31.0	5.3	2.71	1.53	.23	.27
$NaNO_2$..................	1,377	34.0	6.2	1.68	2.19	.27	.29

* Soil types represented are Decatur clay, Hartsells very fine sandy loam, Norfolk fine sandy loam, Norfolk sandy loam, Cecil clay, and Orangeburg fine sandy loam.

† Base application of 600 pounds of 6–10–4 per acre to the cotton and 6–5–2 to the corn annually.

‡ The average pH of the soils at the beginning of the experiment was 6.08.

§ The average exchange capacity of the soils at the end of the experiments was 6.51 m.e. per 100 gm.

TABLE 2

Effect of different sources of nitrogen on yield of seed cotton and on chemical composition of soil

Averages of results from two experiments at two locations*

FERTILIZER TREATMENT†	AVERAGE YIELD OF SEED COTTON PER ACRE, 1928 TO 1941	pH OF SOIL AT END OF EXPERIMENT‡	EXCHANGEABLE CATIONS PER 100 GM. SOIL AT END OF EXPERIMENT§			
			H	Ca	Mg	K
	lbs.		m.e.	m.e.	m.e.	m.e.
No nitrogen................	384	6.1	1.41	2.09	.19	.21
$(NH_4)_2SO_4$................	1,035	5.6	2.23	1.06	.19	.19
$NaNO_3$......................	1,231	6.7	1.14	2.41	.25	.32
¼ $(NH_4)_2SO_4$ + ¾ $NaNO_3$....	1,261	6.2	1.73	1.84	.20	.27

* Soil types represented are Norfolk sandy loam and Cecil clay.

† Base application of 600 pounds of 6–10–4 per acre annually.

‡ The average pH of the soils at the beginning of the experiment was 6.15.

§ The average exchange capacity of the soils at the end of the experiment was 5.78 m.e. per 100 gm.

In table 5 are given the data on several combinations of sources of nitrogen. A combination of one fourth of the nitrogen in the form of ammonium sulfate applied ahead of planting and three fourths in the form of sodium nitrate applied as a side-dressing produced the greatest yield. These data agree with the re-

TABLE 3

Effect of different sources of nitrogen on yields of seed cotton and corn and on chemical composition of soil

Averages of results from three experiments at three locations*

FERTILIZER TREATMENT†	AVERAGE YIELD OF CROPS PER ACRE, 1928 TO 1941		pH OF SOIL AT END OF EXPERIMENT‡	EXCHANGEABLE CATIONS PER 100 GM. SOIL AT END OF EXPERIMENT§			
	Seed cotton	Corn		H	Ca	Mg	K
	lbs.	*bu.*		*m.e.*	*m.e.*	*m.e.*	*m.e.*
No nitrogen..............	832	14.3	5.8	1.80	2.00	.25	.34
$(NH_4)_2SO_4$................	1,381	31.2	5.3	2.61	1.62	.28	.30
Ammo-phos-A............	1,209	29.7	5.5	2.28	1.61	.24	.32
C. S. Meal..............	1,424	27.4	5.8	2.08	2.03	.27	.36
Urea...................	1,443	31.4	5.7	1.96	1.93	.24	.30
Cal-nitro................	1,395	31.4	6.0	1.75	2.30	.25	.31
$Ca(NO_3)_2$................	1,456	34.0	6.0	1.68	2.53	.26	.31
$NaNO_3$.................	1,465	34.6	6.2	1.63	2.25	.26	.31
$CaCN_2$.................	1,364	28.6	6.3	1.53	2.75	.25	.32

* Soil types represented are Hartsells very fine sandy loam, Decatur clay, and Norfolk fine sandy loam.

† Base application of 600 pounds of 6–10–4 per acre to the cotton and 6–5–2 to the corn annually.

‡ The average pH of the soils at the beginning of the experiment was 6.17.

§ The average exchange capacity of the soils at the end of the experiment was 6.72 m.e. per 100 gm.

TABLE 4

Effect of different sources of nitrogen on yields of seed cotton and corn and on chemical composition of soil

Averages of results from five experiments at five locations*

FERTILIZER TREATMENT†	AVERAGE YIELD OF CROPS PER ACRE, 1928 TO 1941		pH OF SOIL AT END OF EXPERIMENT‡	EXCHANGEABLE CATIONS PER 100 GM. SOIL AT END OF EXPERIMENT§			
	Seed cotton	Corn		H	Ca	Mg	K
	lbs.	*bu.*		*m.e.*	*m.e.*	*m.e.*	*m.e.*
No nitrogen..............	653	14.3	5.9	1.64	2.04	.23	.29
$(NH_4)_2SO_4$................	1,262	31.2	5.4	2.46	1.39	.24	.25
Ammo-phos-A............	1,102	29.7	5.6	2.28	1.48	.23	.29
Urea...................	1,371	31.4	5.8	1.91	1.74	.23	.29
$Ca(NO_3)_2$................	1,362	34.0	6.2	1.46	2.58	.24	.31
$NaNO_3$.................	1,371	34.6	6.4	1.43	2.31	.26	.30
$CaCN_2$.................	1,254	28.6	6.4	1.23	2.93	.20	.27

* Soil types represented are Cecil clay, Norfolk sandy loam, Hartsells very fine sandy loam, Decatur clay, and Norfolk fine sandy loam.

† Base application of 600 pounds of 6–10–4 per acre to the cotton and 6–5–2 to the corn annually.

‡ The average pH of the soils at the beginning of the experiment was 6.16.

§ The average exchange capacity of the soils at the end of the experiment was 6.35 m.e. per 100 gm.

sults presented in table 2. It will be noted, however, that a similar combination of ammo-phos-A and sodium nitrate was not so efficient for producing seed cotton as was the previously described combination. Again, this low yield is believed to be due to a deficiency of sulfur. All other combinations tested produced good yields.

TABLE 5

Effect of different combinations of different sources of nitrogen on yields of seed cotton and corn and on chemical composition of soil

Averages of results from four experiments at four locations*

FERTILIZER TREATMENT†	AVERAGE YIELD OF CROPS PER ACRE, 1928 TO 1941		pH OF SOIL AT END OF EXPERIMENT‡	EXCHANGEABLE CATIONS PER 100 GM. SOIL AT END OF EXPERIMENT§			
	Seed cotton	Corn		H	Ca	Mg	K
	lbs.	bu.		m.e.	m.e.	m.e.	m.e.
No nitrogen......................	756	14.1	5.8	2.19	1.97	.24	.28
(NH₄)₂SO₄........................	1,273	30.8	5.2	3.01	1.69	.21	.28
Ammo-phos-A (under) NaNO₃ (side)...........................	1,262	31.8	5.9	2.28	1.85	.26	.27
C. S. Meal (under) NaNO₃ + (NH₄)₂SO₄ (side).................	1,387	30.6	5.6	2.27	1.91	.25	.28
(NH₄)₂SO₄ + Dolomite‖............	1,377	32.8	5.8	2.26	2.24	.39	.28
(NH₄)₂SO₄ + B. Slag‖.............	1,376	32.4	5.9	2.10	2.88	.27	.26
C. S. Meal (under) NaNO₃ (side).....	1,386	32.8	5.9	2.08	2.07	.26	.28
(NH₄)₂SO₄ (under) NaNO₃ (side)....	1,407	33.3	5.8	2.06	1.91	.23	.26
NaNO₃............................	1,360	33.6	6.1	2.00	2.03	.28	.27
(NH₄)₂SO₄ + B. Slag¶.............	1,318	32.6	6.5	1.64	2.90	.29	.24
NaNO₃ + B. Slag¶................	1,315	33.7	7.0	1.17	3.85	.33	.25

* Soil types represented are Decatur clay, Norfolk fine sandy loam, Hartsells very fine sandy loam, and Orangeburg fine sandy loam.

† Base application of 600 pounds of 6-10-4 per acre to the cotton and 6-5-2 to the corn annually. One fourth of the nitrogen application to the cotton was applied ahead of planting, and the remaining three fourths was applied as a side-dressing. For corn, all the nitrogen was applied as a side-dressing, except ammo-phos-A and cottonseed meal, which were put down ahead of planting.

‡ The average pH of the soils at the beginning of the experiment was 5.98.

‖ Dolomite or basic slag added equivalent to the acidity of the (NH₄)₂SO₄.

¶ Enough basic slag added to supply 60 pounds of P₂O₅ per acre to the cotton and 30 pounds to the corn.

§ The average exchange capacity of the soils at the end of the experiment was 6.71 m.e. per 100 gm.

The effect on yields of liming the land at the rate of 3,000 pounds per acre at the beginning of the experiment and then adding enough lime annually to neutralize the potential acidity of the fertilizer is shown in table 6. In every case the lime increased the yields, but the increase was greatest when the lime was applied with acid-forming fertilizers. For example, lime increased the yield of seed cotton obtained from ammo-phos-A 239 pounds per acre, and from ammo-

nium sulfate 186 pounds; but, when applied with calcium or sodium nitrate, lime increased the yield only about 80 pounds per acre. Part of the increase was

TABLE 6

Effect of different sources of nitrogen, applied with and without dolomite, on yields of cotton and corn and on chemical composition of soil

Averages of results from three experiments at three locations*

FERTILIZER TREATMENT†	AVERAGE YIELD OF CROPS PER ACRE, 1928 TO 1941		pH OF SOIL AT END OF EXPERIMENT‡	EXCHANGEABLE CATIONS PER 100 GM. SOIL AT END OF EXPERIMENT§			
	Seed cotton	Corn		H	Ca	Mg	K
	lbs.	*bu.*		*m.e.*	*m.e.*	*m.e.*	*m.e.*
No nitrogen.................	776	17.9	5.9	1.66	2.08	.25	.27
No nitrogen + Dolomite...........	897	23.0	6.3	1.50	2.78	.32	.26
$(NH_4)_2SO_4$.................	1,342	31.1	5.5	2.25	1.52	.28	.22
$(NH_4)_2SO_4$ + Dolomite............	1,528	35.8	6.0	1.76	2.51	.35	.26
Ammo-phos-A..................	1,177	31.3	5.6	1.99	1.56	.23	.24
Ammo-phos-A + Dolomite.........	1,416	34.5	6.2	1.83	2.50	.35	.26
C. S. Meal.................	1,362	30.2	5.7	1.89	2.37	.26	.28
C. S. Meal + Dolomite............	1,438	33.6	6.1	1.64	2.75	.34	.28
Urea....................	1,425	31.9	5.7	1.75	1.74	.24	.24
Urea + Dolomite................	1,495	35.8	6.2	1.64	2.54	.32	.27
$Ca(NO_3)_2$.................	1,417	33.5	6.1	1.53	2.42	.24	.25
$Ca(NO_3)_2$ + Dolomite............	1,505	36.0	6.4	1.41	3.04	.34	.27
$NaNO_3$...................	1,427	33.6	6.3	1.48	2.23	.27	.24
$NaNO_3$ + Dolomite...............	1,496	34.6	6.5	1.38	3.03	.36	.26
$CaCN_2$....................	1,354	29.7	6.3	1.43	2.88	.25	.25
$CaCN_2$ + Dolomite...............	1,445	33.2	6.7	1.25	3.33	.32	.24
Av.—without Dolomite..........	1,285	29.9	5.9	1.75	2.10	.25	.25
Av.—with Dolomite.............	1,403	33.3	6.3	1.55	2.81	.34	.26

* Soil types represented are Norfolk sandy loam, Decatur clay, and Norfolk fine sandy loam.

† Base application of 600 pounds per acre of 6–10–4 to the cotton and 6–5–2 to the corn annually. Limed plots received 3,000 pounds of dolomite per acre when the experiment was started, and thereafter dolomite equivalent to the acidity of the fertilizer applied was added annually.

‡ The average pH of the soils at the beginning of the experiment was 6.10.

§ The average exchange capacity of the soils at the end of the experiment was 6.51 m.e. per 100 gm.

undoubtedly due to magnesium in the dolomite, since dolomite gave an increase when applied with calcium cyanamid.

EFFECT OF DIFFERENT SOURCES OF NITROGEN ON CHEMICAL COMPOSITION OF SOIL

Effect on soil pH

Continuously cropping the soils at all locations for 11 to 13 years without the addition of nitrogen but with the addition of phosphorus and potassium caused an average drop in the pH value of 0.21 (tables 1 to 6). When ammonium sulfate was applied to soils for 11 to 13 years, equivalent to 36 pounds of nitrogen per acre per year, the average soil reaction dropped 0.51 pH. This was the greatest average drop in pH resulting from the application of the different nitrogenous fertilizers used in this experiment. A mixture in which three fifths of the nitrogen was in the form of sodium nitrate and two fifths in the form of ammonium sulfate, was effective in maintaining a constant soil reaction (table 2). Sodium nitrate, because of the strong sodium ion, caused an average increase of 0.42 pH. The greatest average increase in pH was 0.47, which was caused by the application of calcium cyanamid. Of the remaining sources of nitrogen tested, ammo-phos-A, urea, and cottonseed meal made the soils more acid in reaction; but, cal-nitro and calcium nitrate made them more alkaline (tables 3 to 6).

An attempt was made to find combinations of sources of nitrogen that would not materially alter soil reaction. The data in table 5 reveal that the following combinations are nonacid forming: one fourth of the nitrogen as ammo-phos-A and three fourths as sodium nitrate; one fourth as cottonseed meal and three fourths ad sodium nitrate; and one fourth as ammonium sulfate and three fourths as sodium nitrate. A mixture in which one fourth of the nitrogen was cottonseed meal, three eighths ammonium sulfate, and three eighths sodium nitrate was found to be slightly acid forming. Dolomite or basic slag added in amounts equivalent to the acidity of ammonium sulfate, as measured by Pierre (12), was found to be effective in maintaining a constant pH over a 13-year period; but when basic slag containing 8 per cent P_2O_5 was added in amounts great enough to supply 60 pounds of P_2O_5 per acre, the pH was greatly increased. In some cases the soils actually became alkaline in the 11- to 13-year period of treatment when basic slag was used as the source of phosphorus.

At three locations the soils were limed with 3,000 pounds per acre of dolomite at the beginning of the experiment and then only enough dolomite was added annually thereafter to neutralize the potential acidity of the fertilizers used. The results presented in table 6 show that the addition of the lime caused an increase in the pH of all the soils for all the fertilizer treatments when compared to the corresponding plot that received no nitrogen and no lime.

Detailed pH data for each plot in each tier are given in table 7.

Effect on exchangeable hydrogen

For the most part, the amount of exchangeable hydrogen found in the soils was inversely proportional to the pH, but the quantity was affected by the nature of

TABLE 7

pH of soils after treatment annually for 11 to 13 years with different fertilizers

SOIL TREATMENT*	NORFOLK SANDY LOAM	CECIL CLAY	ORANGEBURG FINE SANDY LOAM	DECATUR CLAY		NORFOLK FINE SANDY LOAM		HARTSELLS VERY FINE SANDY LOAM	
	Tier SN	Tier SN	Tier 3	Tier 3	Tier 7	Tier 8	Tier 10	Tier 3	Tier 5
	pH	pH	pH	pH	pH	pH	pH	pH	pH
No nitrogen	5.9	6.2	5.5	5.9	6.1	5.8	5.9	5.7	5.8
No nitrogen + lime†	6.2	...	...	6.3	...	6.4	...	...	...
$NaNO_3$	6.4	6.9	5.6	6.3	6.5	6.1	6.2	6.2	6.0
$NaNO_3$ + lime†	6.5	...	...	6.6	...	6.5	...	...	...
$(NH_4)_2SO_4$	5.5	5.6	4.9	5.6	5.7	5.3	5.2	5.1	5.0
$(NH_4)_2SO_4$ + lime†	6.1	...	...	6.0	...	5.8	...	...	...
Ammo-phos-A	5.4	5.9	...	5.6	...	5.7	...	5.3	...
Ammo-phos-A + lime†	6.1	...	...	6.1	...	6.4	...	...	...
Cottonseed meal	5.7	...	...	5.8	...	5.7	...	5.8	...
Cottonseed meal + lime†	5.9	...	...	6.2	...	6.1	...	...	...
Urea	5.7	6.2	...	5.7	...	5.7	...	5.7	...
Urea + lime†	6.1	...	...	6.2	...	6.4	...	...	...
Cal-nitro	...	...	...	6.2	...	5.9	...	5.9	...
Cal-nitro + lime†	...	...	...	6.4	...	6.4	...	...	...
$Ca(NO_3)_2$	6.3	6.7	...	6.0	...	5.9	...	6.2	...
$Ca(NO_3)_2$ + lime†	6.6	...	...	6.3	...	6.4	...	...	...
$CaCN_2$	6.3	6.8	...	6.2	...	6.3	...	6.4	...
$CaCN_2$ + lime†	7.0	...	...	6.5	...	6.7	...	...	...
$(NH_4)_2SO_4$ + dolomite‡	6.1	6.2	5.4	...	6.1	...	6.0	...	5.8
$(NH_4)_2SO_4$ + B. Slag‡	7.3	7.8	5.7	...	6.1	...	5.8	...	5.8
$(NH_4)_2SO_4$ + B. Slag§	...	...	5.9	...	6.4	...	6.8	...	6.8
$NaNO_3$ + B. Slag§	...	...	6.6	...	7.2	...	7.0	...	7.4
$\frac{2}{3}(NH_4)_2SO_4 + \frac{1}{3}NaNO_3$	6.0	6.3	...	...	...	...	...	...	...
¼ Ammo-phos-A + ¾ $NaNO_3$	...	...	5.5	...	6.3	...	6.2	...	5.8
¼ Cottonseed meal + ⅜ $NaNO_3$ + ⅜ $(NH_4)_2SO_4$	...	...	5.3	...	6.0	...	5.4	...	5.6
¼ Cottonseed meal + ¾ $NaNO_3$	...	...	5.6	...	6.2	...	6.2	...	5.8
¼ $(NH_4)_2SO_4$ + ¾ $NaNO_3$	...	...	5.4	...	6.1	...	5.8	...	5.7
$\frac{2}{3}(NH_4)_2SO_4 + \frac{1}{3}NaNO_3$ + lime†	6.1	...	...	...	...	...	...	...	...

* Rates of phosphorus and potassium applied to the different tiers is given in the footnotes of tables 1 to 6 inclusive.

† Plots received 3,000 pounds of lime per acre when the experiment was started, and thereafter annual additions equivalent to the acidity of the fertilizer applied.

‡ Dolomite or basic slag added equivalent to the acidity of the fertilizer applied.

§ Basic slag added equivalent to 45 pounds of P_2O_5 per acre annually.

the soil. Thus, as would be expected, the acid-forming fertilizers increased the amount of exchangeable hydrogen in proportion to the acidity of the fertilizers, and, conversely, the basic fertilizers decreased the quantity of exchangeable hydrogen in proportion to the basicity of the fertilizers. Ammonium sulfate, for example, increased the exchangeable hydrogen content of all soils studied by an average of 0.78 m.e. 100 gm. of soil, urea increased it by 0.17 m.e., sodium nitrate decreased it by 0.21 m.e., and calcium cyanamid decreased it by 0.34 m.e.

TABLE 8

Effect of different sources of nitrogen, applied with and without lime, on yields of seed cotton and corn and on chemical composition of Decatur clay at the Tennessee Valley Substation, Belle Mina, Alabama

SOURCES OF N AND OTHER SPECIAL TREATMENTS*	AVERAGE YIELD OF CROPS PER ACRE, 1929 TO 1939				pH OF SOIL IN 1939 (3)†		EXCHANGEABLE CATIONS PER 100 GM. SOIL IN 1939‡							
	Seed cotton		Corn				H		Ca		Mg		K	
	Unlimed	Limed§	Unlimed	Limed	Unlimed	Limed	Unlimed	Limed	Unlimed	Limed	Unlimed	Limed	Unlimed	Limed
	lbs.	lbs.	bu.	bu.			m.e.	m.e.	m.e.	m.e.	m.e.	m.e.	m.e.	m.e.
No nitrogen...........	1,157	1,238	24.1	28.3	5.9	6.3	2.65	2.58	3.87	5.18	.59	.59	.60	.58
$(NH_4)_2SO_4$............	1,555	1,596	37.9	40.6	5.6	6.0	3.15	3.01	3.50	4.68	.66	.66	.51	.57
$(NH_4)_2SO_4$ (under)....	1,487	1,572	39.7	41.5	5.6	6.0	3.05	3.08	3.67	4.66	.83	.69	.51	.59
$(NH_4)_2HPO_4$ (under)..	1,519	1,575	36.6	39.6	5.6	6.1	2.82	3.10	3.40	4.43	.57	.60	.54	.57
C. S. Meal (under)....	1,499	1,558	36.4	39.3	5.8	6.2	2.76	2.79	3.93	4.51	.58	.62	.62	.62
Urea................	1,553	1,605	38.1	41.8	5.7	6.2	2.68	2.69	3.66	4.34	.53	.52	.51	.58
Cal-nitro............	1,556	1,585	38.0	40.3	6.2	6.4	2.56	2.50	4.50	5.41	.54	.66	.53	.58
$CaCN_2$ (under)........	1,504	1,602	37.0	40.6	6.2	6.5	2.49	2.42	4.92	5.52	.56	.62	.53	.57
$Ca(NO_3)_2$............	1,547	1,597	40.2	42.4	6.0	6.3	2.31	2.45	4.31	5.36	.53	.55	.54	.59
$NaNO_3$ (under).......	1,566	1,589	39.5	40.8	6.2	6.4	2.25	2.41	4.13	5.35	.54	.61	.52	.57
$NaNO_3$...............	1,576	1,621	40.1	41.0	6.3	6.6	2.24	2.37	4.20	5.37	.63	.65	.52	.58

* The base application was 600 pounds of 6-10-4 per acre to the cotton and 6-5-2 to the corn annually. "Under" indicates that all the nitrogen was applied ahead of planting; in all other cases, one fourth of the nitrogen was applied to the cotton ahead of planting and three fourths was applied as a side-dressing; for corn, all was applied as a side-dressing.

† The pH of the soil at the start of the experiment was 6.3.

‡ The average exchange capacity of the soil was 11.63 m.e. per 100 gm. at the end of the experiment.

§ Limed with 3,000 pounds of dolomite at the start of the experiment and then annually thereafter with dolomite equivalent to the acidity of the fertilizer.

Effect on exchangeable calcium

The amount of exchangeable calcium found in the soils was inversely proportional to the amount of exchangeable hydrogen, except where a fertilizer was added that contained calcium. In such cases the calcium was found to be higher than would be indicated from the pH and content of exchangeable hydrogen (note the data for calcium cyanamid and sodium nitrate in table 4). It is also apparent that maintaining the pH at 5.8 or 5.9 by the use of different combinations of

fertilizer and liming materials (table 5) does not mean that the amount of exchangeable calcium is being held constant, even though the pH and exchangeable hydrogen are held nearly constant. Adding basic slag or dolomite in quantities sufficient to maintain a constant pH of the soil actually resulted in an increase in the amount of exchangeable calcium in the soil. The addition of sodium nitrate as a source of nitrogen resulted in a higher content of exchangeable calcium in the soil after 11 to 13 years than was found in the same soils where no nitrogen was added. However, the use of sodium nitrate to neutralize acidity always left the soils lower in exchangeable calcium than when lime or slag was used. This

TABLE 9

Effect of different sources of nitrogen, applied with and without lime, on yields of seed cotton and corn and on chemical composition of Norfolk fine sandy loam at the Wiregrass Substation, Headland, Alabama

SOURCES OF N AND OTHER SPECIAL TREATMENTS*	AVERAGE YIELD OF CROPS PER ACRE, 1930 TO 1939				pH OF SOIL IN 1939†		EXCHANGEABLE CATIONS PER 100 GM. SOIL IN 1939‡							
	Seed cotton		Corn				H		Ca		Mg		K	
	Unlimed	Limed§	Unlimed	Limed	Unlimed	Limed	Unlimed	Limed	Unlimed	Limed	Unlimed	Limed	Unlimed	Limed
	lbs.	lbs.	bu.	bu.			m.e.	m.e.	m.e.	m.e.	m.e.	m.e.	m.e.	m.e.
No nitrogen	765	1,001	11.8	17.8	5.8	6.4	1.45	1.24	1.19	1.88	.11	.29	.11	.11
$(NH_4)_2SO_4$ (under)	1,310	1,473	25.1	29.2	5.4	6.1	2.43	1.23	1.10	1.51	.13	.28	.10	.11
$(NH_4)_2SO_4$	1,382	1,596	24.4	31.1	5.3	5.9	2.40	1.44	.65	1.63	.12	.30	.09	.11
$(NH_4)_2HPO_4$ (under)	1,087	1,425	26.1	29.4	5.7	6.4	1.82	1.52	.95	1.86	.08	.31	.10	.13
C. S. Meal (under)	1,410	1,563	24.1	27.9	5.7	6.1	1.81	1.29	1.22	2.10	.17	.26	.12	.11
Urea	1,428	1,537	25.7	29.8	5.7	6.4	1.63	1.38	1.20	1.90	.14	.28	.10	.15
$NaNO_3$ (under)	1,326	1,538	26.1	27.6	5.9	6.5	1.57	1.37	1.23	2.10	.13	.28	.09	.11
$Ca(NO_3)_2$	1,460	1,582	27.2	29.6	5.9	6.4	1.55	1.11	1.77	1.92	.14	.27	.10	.12
$NaNO_3$	1,437	1,593	27.7	28.2	6.1	6.5	1.49	1.06	1.24	2.35	.10	.32	.09	.09
Cal-nitro	1,341	1,464	24.5	28.1	5.9	6.4	1.46	.97	1.25	2.20	.10	.35	.08	.10
$CaCN_2$ (under)	1,371	1,543	22.4	25.8	6.3	6.7	1.20	.86	1.60	2.48	.12	.23	.10	.09

* See corresponding footnote to table 8.

† The pH of the soil at the start of the experiment was 5.9.

‡ The exchange capacity of the soil was 4.87 m.e. per 100 gm. at the end of the experiment.

§ Limed with 3,000 pounds of dolomite at the start of the experiment and then annually thereafter with dolomite equivalent to the acidity of the fertilizer.

would be an important factor in correcting the acidity of soils low in available calcium.

The addition of 3,000 pounds of dolomite per acre at the beginning of the experiment and the annual application thereafter or dolomite equivalent to the acidity of the fertilizer caused a large increase in the amount of exchangeable calcium found in all soils (table 6). The average increase was 0.71 m.e. per 100 gm. of soil, with a corresponding decrease of 0.20 m.e. of exchangeable hydrogen per 100 gm. The only acid-forming fertilizer that did not cause a reduction in the amount of exchangeable calcium in the soils was cottonseed meal. This may have been due to the calcium in the meal.

Effect on exchangeable magnesium

There is no evidence in the data (tables 1 to 6) that the different sources of nitrogen appreciably affected the exchangeable magnesium content of the soils. Neither was the exchangeable magnesium content related to the pH, exchangeable hydrogen, or exchangeable calcium in the soils studied. The only effect observed was that dolomite added to the soils caused an average increase of 0.09 m.e. of exchangeable magnesium per 100 gm. of soil. Many of the soils of southeastern United States are known to be deficient in magnesium, and on such soils the use of dolomite should be preferred as a liming material.

Effect on exchangeable potassium

A study of all the data in tables 1 to 6 indicates that the different sources of nitrogen and other variations in fertilizer treatment and liming had little or no effect on the amount of exchangeable potassium found in the soil after 11 to 13 years of fertilizer treatment and crop production. The limed plots, (table 6) apparently contained a little more exchangeable potassium than the unlimed plots at the end of the 11- to 13-year period. The difference, however, amounted to less than 20 pounds of potassium per acre in most cases. On the other hand, the results indicate that plots treated with ammonium sulfate contained less exchangeable potash than those treated with other sources of nitrogen, but again the differences usually amounted to less than 20 pounds of potassium per acre.

Detailed data for two of the soils representing extremes in chemical composition and fertility are given in tables 8 and 9.

VARIATIONS IN pH AND AMOUNTS OF VARIOUS CATIONS IN SOIL FROM ROWS AND FROM MIDDLES

On much of the land in southern United States the fertilizer is placed in a band and the crop planted above it in exactly the same place year after year. This condition is the result of contour farming and of a system involving largely cotton and corn. Since the system of placing the cotton and corn rows in the same place each year was used in this study, two tiers of plots were sampled to compare the chemical composition of the soil in the rows with that in the middles. The method of sampling has been described.

In general, the data in table 10 show that, when acid-forming fertilizers were used on Hartsells very fine sandy loam, the soil from the rows had a lower pH and a higher content of exchangeable hydrogen than did the middles. The greatest differences were obtained where basic slag, calcium cyanamid, ammonium sulfate, or diammonium phosphate was applied.

The content of exchangeable calcium was higher in nearly every case in the soil from the middles, except where calcium-containing sources of nitrogen were applied under the crop in bands. Exchangeable magnesium was found in greater quantities in the middles than in the rows.

In tier 5, the amount of exchangeable potassium was found to be higher in the rows than in the middles, but the reverse was apparent in tier 3. The differences in either case, however, are too small to be of significance.

TABLE 10

Comparison of the chemical composition of soil taken from crop rows and from middles (midway between the rows) after different fertilizers had been applied in bands in the rows annually for 15 years*

Hartsells very fine sandy loam, Sand Mountain Substation—rotation of cotton and corn

SOURCES OF N AND OTHER SPECIAL TREATMENTS†	pH OF THE SOIL AT END OF EXPERIMENT‡		EXCHANGEABLE CATIONS PER 100 GM. SOIL AT END OF EXPERIMENT§							
			H		Ca		Mg		K	
	Row	Middle	Row	Mid-dle	Row	Mid-dle	Row	Mid-dle	Row	Mid-dle
			m.e.	m.e.	m.e.	m.e.	m.e.	m.e.	m.e.	m.e.
Results from tier 5										
No nitrogen..................	5.8	5.8	1.16	1.30	0.86	0.98	.07	.09	.32	.24
(NH₄)₂SO₄....................	4.9	5.0	1.90	1.83	0.48	0.56	.04	.05	.31	.26
Ammo-phos-A (under) NaNO₃ (side).....................	5.7	5.5	1.70	1.67	0.69	0.86	.07	.07	.26	.25
(NH₄)₂SO₄ + Dolomite‖.......	5.6	5.7	1.43	1.30	1.00	1.10	.09	.18	.30	.24
C. S. Meal (under) NaNO₃ + NH₄)₂SO₄ (side)............	5.6	5.6	1.38	1.27	0.79	0.88	.05	.06	.31	.25
(NH₄)₂SO₄ (under) NaNO₃ (side)......................	5.8	5.8	1.26	1.27	0.85	0.94	.05	.05	.30	.26
(NH₄)₂SO₄ + B. Slag‖........	5.8	6.0	1.17	1.20	1.21	1.36	.08	.08	.28	.22
NaNO₃.......................	6.2	6.0	0.90	1.17	1.16	1.20	.06	.10	.29	.24
C. S. Meal (under) NaNO₃ (side)......................	6.0	5.9	0.87	1.03	1.42	1.01	.06	.09	.31	.26
(NH₄)₂SO₄ + B. Slag¶........	7.2	6.2	0.25	0.80	2.40	1.44	.07	.11	.29	.24
NaNO₃ + B. Slag¶..........	7.7	6.5	0.15	0.58	3.52	1.92	.13	.14	.28	.24
Results from tier 3										
No nitrogen..................	5.7	5.7	1.29	1.34	1.05	0.83	.07	.09	.32	.33
(NH₄)₂SO₄ (under)...........	4.8	5.2	2.46	2.13	0.64	0.78	.03	.08	.26	.34
(NH₄)₂SO₄....................	4.8	5.4	2.46	1.95	0.50	0.50	.03	.08	.25	.31
(NH₄)₂HPO₄ (under).........	5.1	5.5	2.23	2.03	0.39	0.51	.04	.09	.30	.34
urea........................	5.6	5.8	1.57	1.40	0.93	0.89	.03	.08	.29	.30
C. S. Meal (under)...........	5.7	5.7	1.53	1.40	1.28	1.05	.08	.09	.31	.37
Cal-nitro....................	5.9	5.8	1.43	1.23	1.33	1.06	.09	.12	.28	.39
NaNO₃ (under)..............	6.0	6.1	0.93	1.13	1.28	1.01	.05	.10	.29	.29
Ca(NO₃)₂....................	6.0	5.9	1.13	1.23	1.67	1.30	.08	.11	.29	.30
NaNO₃.......................	6.2	6.1	0.86	1.13	1.39	1.10	.05	.09	.29	.30
CaCN₂ (under)...............	6.5	6.2	0.67	0.93	2.08	1.48	.09	.08	.30	.31

* The rows of cotton and corn were in the same location every year, as were the bands of fertilizer. The only distribution of fertilizer to the middles was brought about by cultivation or the application of fertilizer as a side-dressing.

† The base application to all plots was 600 pounds of 0-10-4 per acre annually to the cotton and 600 pounds of 0-5-2 to the corn. Nitrogen was applied in the forms shown at the rate of 36 pounds per acre, one fourth under the cotton and three fourths as a side-dressing. All nitrogen was applied to corn as a side-dressing except ammo-phos-A and cottonseed meal, which were applied ahead of planting.

‡ The pH of the soil at the start of the experiment was 6.0 for both tiers.

§ The exchange capacity of the soil at the close of the experiment was 3.86 m.e. per 100 gm. for tier 5 and 3.67 m.e. for tier 3.

‖ Dolomite or basic slag added annually equivalent to the acidity of the fertilizer.

¶ Enough basic slag added to supply 60 pounds of P_2O_5 per acre to the cotton and 30 pounds to the corn.

These data indicate that extreme care must be exercised in sampling land where the fertilizer has been applied in bands in relatively the same position year after year.

SUMMARY

Fertility plots established in Alabama in the period 1928 to 1930 were studied to determine the long-time effect of various sources of nitrogen on the chemical composition of several soils and on the yields of seed cotton and corn. Samples of soils taken from the plots of the nine different sites in 1941 were analyzed for soil reaction, and for exchangeable hydrogen, calcium, magnesium, and potassium. The results of the investigation may be summarized as follows:

On most sities, the nonacid-forming sources of nitrogen, except cyanamid, were definitely superior to the acid-forming sources for the production of cotton and corn when acidity was not corrected. The nonacid-forming sources produced an average of about 100 pounds of seed cotton and 3 bushels of corn more per acre. When the acidity of the acid-forming fertilizers was corrected, these differences were eliminated at most sites. Calcium cyanamid gave inferior results at most sites.

Ammo-phos-A produced distinctly lower yields of seed cotton than did ammonium sulfate, even though the latter made the soil more acid. It is believed that the sulfur in ammonium sulfate was responsible for the difference in yields.

A mixture consisting of three-fifths to three-fourths of the nitrogen as sodium nitrate and two-fifths to one-fourth as ammonium sulfate gave the greatest average returns of seed cotton. Sodium and sulfur may have been responsible for the increase. However, the difference in returns between this mixture and some other sources of nitrogen were not great.

Dolomite added to acid-forming fertilizers increased the average yield of seed cotton 143 pounds per acre and of corn 3.8 bushels per acre over an 11- to 13-year period, and, when added to nonacid-forming fertilizers, it increased the average yield of seed cotton 83 pounds per acre and of corn 2.3 bushels. Part of the increase was undoubtedly due to magnesium in the dolomite.

Continuous cropping for 11 to 13 years at all locations without the addition of lime or nitrogen caused an average drop in soil pH of only 0.21.

Ammonium sulfate, ammo-phos-A, urea, and cottonseed meal decreased the pH and increased the amount of exchangeable hydrogen of the soil in proportion to the acidity of the fertilizers.

Calcium nitrate, sodium nitrate, calcium cyanamid, and cal-nitro increased the pH and decreased the amount of exchangeable hydrogen in the soil in proportion to the basicity of the fertilizers.

Additions of dolomite or basic slag, in amounts equivalent to the acidity of the fertilizer, maintained the soil at a constant pH value and a constant level of exchangeable hydrogen, but they increased slightly the amount of exchangeable calcium.

Additions of basic slag equivalent to 60 pounds of P_2O_5 per acre caused big increases in pH and exchangeable calcium in the soil and large decreases in exchangeable hydrogen.

Sodium nitrate was effective in maintaining a constant pH in the soil when about three-fourths of the nitrogen was added as sodium nitrate and one-fourth as an acid-forming source of nitrogen; but the exchangeable calcium was materially lower than when lime or slag was used to neutralize the acidity.

An increase in the exchangeable hydrogen in the soil was usually accompanied by a decrease in exchangeable calcium and *vice versa*, but there appeared to be little or no relation between exchangeable hydrogen and the amount of exchangeable magnesium or potassium.

The addition of calcium nitrate, cal-nitro, or calcium cyanamid increased the amount of exchangeable calcium in the soil.

The use of dolomite as a liming material caused a considerable increase in the exchangeable magnesium content of the soils.

For the soils studied, 3,000 pounds of dolomite applied at the beginning of the experiment, with annual applications thereafter equivalent to the potential acidity of the fertilizer, caused an average increase in exchangeable calcium of 33 per cent, an increase in exchangeable magnesium of 36 per cent, a slight increase in exchangeable potassium, a decrease in exchangeable hydrogen of 11 per cent, and an increase in pH of 7 per cent.

Apparently, the only fertilizer treatment that appreciably affected the exchangeable magnesium content of the soils was the addition of materials containing magnesium, in which case the amount of magnesium was always increased.

Ammonium sulfate caused a slight decrease in the exchangeable potash in the soil.

Analyses of samples of soil taken from the crop rows as compared to analyses of soils taken from the middles (half way between the rows) showed that:

(a) When acid-forming fertilizers were applied in the rows, the soil from the rows was lower in pH, higher in exchangeable hyrdogen, and lower in calcium than the sample taken from the middles.

(b) The exchangeable calcium content of the middles was almost always higher than that of the rows, except where a calcium-containing fertilizer was added in the row.

(c) Exchangeable magnesium was found in greater quantities in the middles than in the rows where magnesium was not added to the soil.

(d) In one tier of plots the amount of exchangeable potassium was found to be higher in the row than in the middle (all potash was applied in the row), while in the other tier just the reverse was found.

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